A THEORY OF TANNING

Based Upon the Study of Tanning Effects of Naphthalene Derivatives and Other Organic Compounds

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1928

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY

BY

YUN HUA LI, B.S., CH.E.

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To the Memory of My Father

Wen Yee Li

This Work is Affectionately Dedicated.

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[Reprinted from the Journal of the American Leather Chemists Association, August, 1927.]

A Theory of Tanning

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By Yun Hua Li, B.S., CH.E.

Historical Review of Synthetic Tanning Materials

The history of tanning dates back into prehistoric ages, but it was in about 1660 that the first scientific paper on tanning entitled "Oak Prepared for Tanning" was published in the Philosophical Transactions of the Royal Society.[1] Since then, scientists began to study what is really contained in oak and other wood extracts. According to Nierenstein,[2] gallotannin was first isolated by W. Lewis in 1763; this was followed by the discovery of gallic acid in 1768 by Piepenbring. In 1787 Scheele[3] obtained gallic acid in fermented gall extracts, and in the same year Kunzemüller[4] separated gallic acid as a crystalline body from oak galls. While the determination of the composition of gallotannin was going on, Resch[5] in 1801 started to use organic material other than oak. He was the first to conduct tanning experiments, using three parts of

* Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the faculty of Pure Science of Columbia University.

[1] Seymour-Jones, F. L., *J. Soc. Leather Trades Chem.*, **8**, 173-4 (1924).

[2] Nierenstein, M., *J. Soc. Chem. Ind.*, **41**, 29-30T (1922).

[3] Scheele, *Greil's Chem. Ann.*, **3**, 1 (1787).

[4] Kunzemüller, *Ibid.*, **3**, 413 (1787).

[5] Resch, *Scherer's Jour.*, **6**, 495 (1801).

peat and one part of oak bark. By the action of nitric acid on substances of vegetable and animal origin, Hatchet[6] in 1805, Chevreul[7] in 1810 and Vogel[8] in 1812 claimed to have obtained tanning materials. By subsequent treatment with lime and soot or tar Ashmore[9] in 1833 claimed to have converted pelt into leather. By treating peat with nitric acid Jennings[10] in 1858 obtained some artificial tanning material. Skey[11] in 1866 by treating bituminous coal or lignite with nitric acid obtained a dark brown extract, soluble in water and having the ability of precipitating gelatine. Although many artificial tanning materials had been produced up to this time, they could not be considered as "synthetic tannins," because their compositions had never been determined. However, through these suggestions, Schiff[12] in 1871 obtained a digallic acid which he claimed to be identical with the natural tannin. Later it was proved by Flawitski[2] (1895) and by Walden[2] (1898) that Schiff's digallic acid is not tannin. Böttinger[13] heated gallic acid with glyoxylic acid and obtained a product which showed characteristics of tannin but which was by no means identical with it. Perhaps the most elaborate work on synthetic tannins is that of Fischer and Freundenberg[14] who published a series of articles in *Berichte.* Fischer and Bergmann[15] succeeded in preparing penta-m-digalloyl-b-glucose which they proved to be an isomer of tannin obtained from Chinese nutgalls, and is now considered as nearest to the natural tannin.

Depsides.—Klepl[16] was the first to synthesize the so-called di- and tridepsides by simply heating p-hydroxybenzoic acid. A better method, however, was developed by Fischer and Freundenberg.[17] According to their method, if the chlorides of carbomethoxy (or carbethoxy) hydroxy benzoic acids are coupled with

[6] Hatchett, *Gehlen's Jour.*, **1**, 545 (1805).
[7] Chevreul, *Ann. Chim.*, **73**, 36 (1810).
[8] Vogel, *Jour. Chem. Phys.*, **6**, 101 (1812).
[9] Ashmore, *Dingler's Jour.*, **48**, 67 (1833).
[10] Jennings, *Jahresber. d. Chem.* (1858), 666.
[11] Skey, *Chemical News* (1866) 206; *Zeit. f. Chem.* **9**, 753 (1866).
[12] Schiff, *Ber.*, **4**, 231 and 967 (1871).
[13] Böttinger, *Ber.*, **17**, 1503 (1884).
[14] Fischer and Freundenberg, *Ber.*, **45**, 915-35; 2709-26, (1912); *Ber.*, **46**, 1116-38, (1913).
[15] Fischer and Bergmann, *Ber.*, **51**, 1760 (1918).
[16] Klepl, *Jour. pr. Chem.*, **28**, 208 (1883).
[17] Fischer and Freundenberg, *Liebig's Ann.*, **372**, 32 (1909).

the sodium salts of hydroxy-benzoic acids, esters are formed according to the reaction:

$$CH_3COO.O.C_6H_4COCl + NaO.C_6H_4COONa = CH_3COO.O.C_6H_4CO.O.C_6H_4COONa + NaCl$$

On hydrolysis of the esters, these are converted into the corresponding hydroxy derivatives, $HO.C_6H_4CO.O.C_6H_4COOH$. Fischer and Freundenberg[14] prepared a number of the depsides, di-, tri- and polydepsides, which in some cases showed remarkable tanning effects.

Neradols.—Early in 1872, von Baeyer[18] observed that when pyrogallol was treated with formaldehyde, a product was obtained which precipitated gelatine. The practical conversion of the condensation products of phenol derivatives and formaldehyde was first effected by Stiasny, who obtained a German Patent 262,558 (1911) to manufacture this type of tanning materials. The Neradol D[19] on the market is a condensation product of cresolsulfonic acid and formaldehyde. With formaldehyde, naphthol[20] derivatives also enter into the reaction. Higher hydrocarbons, such as anthracene, retene, and sulfonated tar oils, can also be similarly condensed.

Other Condensation Products.—Many aromatic hydroxy compounds condense without addition of any condensing agents. When phenol-sulfonic acid is heated in vacuo at 130° C., condensation takes place[21] with two residues of phenolsulfonic acid in the molecule. The aromatic dihydric alcohols condense with the aromatic sulfonic acids with great ease,[22] even liberating heat. By the aid of condensing agents, condensations are usually accelerated. In 1873, Schiff[23] obtained a phenolsulfonic acid anhydride, $HO.C_6H_4SO_2.O.C_6H_4SO_3H$, by allowing phosphorus oxychloride to interact with phenolsulfonic acid. Sulphur chloride also induces

[18] von Baeyer, see Nierenstein, *Collegium*, **434**, 236 (1906).
[19] Neradol D., Ger. Pat., 291,457; Austr. Pat., 61,057.
[20] Ger. Pats., 293,042; 293,640; 293,693; 303,640.
[21] Austr. Pat. 64,479.
[22] Grasser's Book, "Synthetic Tannin." The English translation by Enna (1922) p. 51-52. D. van Nostrand Co., New York.
[23] Schiff, *Liebig's Ann.*, **170**, 43 (1873).

condensation of phenolsulfonic acid. Arsenious acid[12] and antimonic acid[24] had been early used as condensing agents. All these condensation products possess more or less tanning properties.

Non-Condensed Compounds.—Many organic compounds can be used directly as tanning agents without first subjecting them to any process of condensation. Formaldehyde[25] was used for tanning as early as 1891. Tanning with picric acid[26] was investigated in 1901. Quinone tannage[27] was started in 1907. Numerous compounds of these types have been gaining consideration.

Other materials, such as sulfite pulp waste liquors[28] and the so-called acid rosins from oil refineries have been extensively employed.

Historical Review of Tanning Theories

There are three distinct schools of thought regarding the theories of tanning, that is, colloidal, chemical, and colloid-chemical.

Colloidal Theory.—Knapp[29] (1858) was the first to demonstrate that tanning is a process of colloidal adsorption, in which the fibres of the hide substances are mechanically coated by the tannin particles, so as to prevent them from adhesion and hydration. This idea of tanning was supported by Stiasny.[30] Ricevuto[31] considered that tanning is due to the precipitation of one colloid by another of opposite charge. The hide substance, the collagen, is positively charged and tannin negatively charged in acid solutions, and when these are present in the tan liquor, the tannin naturally migrates to the hide substance for the neutralization of these opposite charges. This view was supported by Raffa.[32]

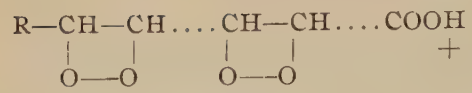
Moeller[33] viewed it from the phenomenon of peptization. In vegetable tans, tannin is the peptizer, while ellagic acid, in the

[24] Biginelli, *Gazz. Chim. ital.*, **39**, 11, 268-89 (1909).
[25] Trillat, M., *Rev. de. Chim. Industrielle*, **10**, (111), 69 (1901).
[26] *Leather Manufacturer*, **12**, (3), 54, (1901).
[27] German Pat. 206,957 (1907).
[28] "Literatur uber Sulfitlauge," 1910-13.
[29] Knapp, F., *Dingler's Polytech. J.*, **149**, 305, 379 (1858).
[30] Stiasny, E., *Chem. Ztg.*, **32**, 539 (1909).
[31] Ricevuto, A., *Z. Chem. Ind. Kolloide*, **3**, 114-7 (1907).
[32] Raffa, E., *Gazz. chim. ital.*, **39**, (1), 28-34 (1909).
[33] Moeller, W., *Collegium*, **548**, 441-57 (1915); **549**, 1-16; 43-50; 125 (1916).

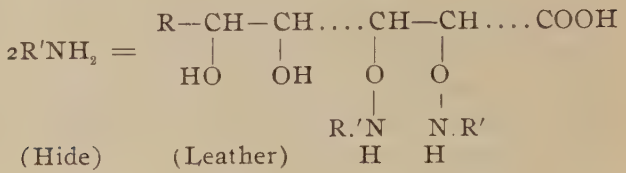
case of gallotannin and phlobaphenes in the case of catechu-tannin are the peptizable substances. The peptizer penetrates with ease the fibres of the skin, forming with them a solid solution without tanning them. The tannage is produced by the peptized substances deposited on the surface of the fibres, the outer layers of which are finally peptized by combining with the peptized substances. Tanning with formaldehyde was considered a colloidal phenomenon by Thuau[34] who pointed out that the tanning effect of formaldehyde is increased by those salts which bring about colloidal polymerization. Moeller[35] making use of his peptization theory considered that formaldehyde is a peptizer and polymerized formaldehyde, which is always formed in the presence of alkali, is a peptizable substance, and therefore formaldehyde will not tan without the presence of polymerized formaldehyde. Only aliphatic aldehydes are capable of forming polymers and therefore tan; aromatic aldehydes do not tan as well, because they do not polymerize.

Chemical Theory.—Seguin[36] (1796) recognized that tanbark contained a "particular principle" which was soluble in water and gave a precipitate with gelatine, and he pointed out that this "principle" fixed itself upon the hide during tannage, effecting a specific combination between tanning material and the hide. The chemical theory of tanning was more extensively studied by Fahrion[37] who considered nearly all kinds of tannages as a chemical process. According to Fahrion, a distinction must be made between primary and secondary tanstuffs. The original tanning material contains the primary tanstuff which by action of air or water is converted into the secondary and real tanning agent. For examples, in oil tannage, the unsaturated fatty acids are the primary tanstuff while a peroxide form of these acids is the secondary and real tanstuff. The tanning occurs when the amino groups of the hide substance combine with the peroxide group of the oil:

[34] Thuau, *Collegium*, (1909) 363, 211.
[35] Moeller, W., *J. Soc. Leather Trades Chem.*, **2**, 188-90 (1918).
[36] Seguin, *Ann. chim.*, **20**, 15 (1797)
[37] Fahrion, W., *Z. angew. Chem.*, **16**, 665 (1903); **22**, 2083-97; 2135-44; 2187-94 (1909).



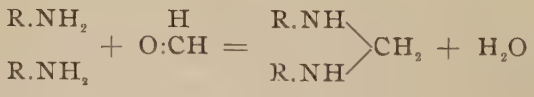
(Peroxide Form of Oil)



(Hide) (Leather)

In the case of aldehyde tannage the formaldehyde is both primary and secondary tanstuff and air is not essential. In vegetable tannage the primary tanstuffs are polyphenols and the secondary the quinones or the oxidation products from polyphenols. In mineral tannages, such as in chrome tanning, the primary tanstuff is $Cr_2(SO_4)_3$ which by hydrolysis becomes a basic salt, the secondary agent. The hide by catalysis dehydrates this, precipitating an insoluble partial anhydride. After deacidification with alkali, the hide itself enters into chemical combination with the precipitated anhydride.

Nierenstein[38] supported Fahrion's theory in many cases, and in case of formaldehyde the reaction may be represented as follows:



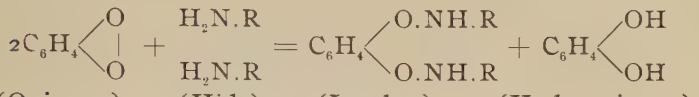
(Hide) (Leather)

The more recent work of Thomas[39] (1926) shows that the combination of formaldehyde and protein is not limited to a single 1:1 ratio, thus giving a methyleneamino linkage with the amino N of the molecule, but a triformal linkage with amino groups is also possible. Fixation may take place with imino groups, so that the protein may combine with relatively large amounts of formaldehyde.

Quinone tannage has been universally accepted as a purely

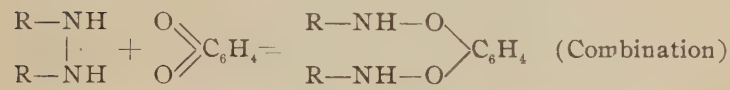
[38] Nierenstein, M., *Collegium*, (1905), 157, 159.
[39] Thomas, A. W., *J. Amer. Leather Chem. Assoc.*, **21**, 57-76 (1926).

chemical process. According to Thuau[34] the chemical combination can be represented as follows:

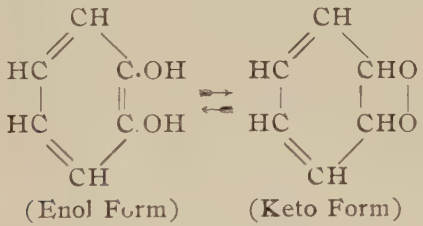


Fahrion[40] suggested somewhat different reactions:

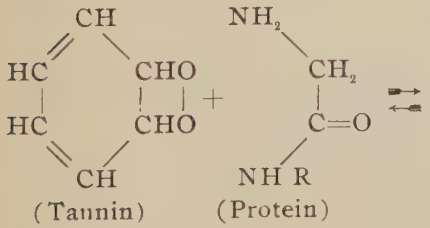
$$2R.NH_2 + O = R\text{–}NH\text{–}NH\text{–}R + H_2O \text{ (Oxidation)}$$



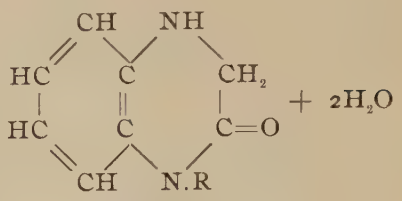
In vegetable tanning, Powarnin[41] objected to the assumption of the formation of quinones by oxidation and suggested that they are formed by a tautomeric change, and this constitutes the "active carbonyl" theory.



The enol form was supposed to be stable chiefly in alkaline solution, and the keto form in acid solution. Only the keto form has tanning properties and the action is represented as follows:



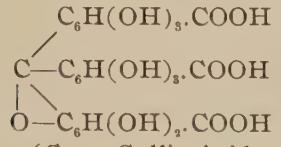
[40] Fahrion, W., *Mon. sci.* (1911), 361; (1914), 112.
[41] Powarnin, G., *Collegium* (1914), 634.



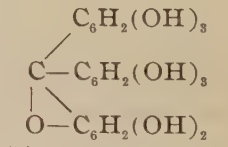
(Leather)

In any case when tanning with quinones, the process is an oxidation. Meunier and Seyewetz[42] found that hydroquinone can be identified in the quinone solution which has been used for tanning. Fahrion[43] also demonstrated that during the quinone tannage, the content of active oxygen in the quinone becomes smaller, and only the amino group of the hide protein can effect this.

Conception of the "Tannophors."—In 1872, von Baeyer[44] found that pyrogallol, when condensed with formaldehyde, yields an amorphous compound which is soluble in water and precipitates gelatin. This observation was confirmed by Caro[45] and by Kahl.[46] Nierenstein[47] repeated the experiments on the one hand with pyrogallol, and on the other with gallic acid, and found that in both cases, together with insoluble diphenylmethane derivatives, soluble compounds, capable of precipitating gelatine were also formed. The soluble compounds from gallic acid was indicated to be hexahydroxy-aurinecarboxylic acid, and that from pyrogallol had a similar structure:



(From Gallic Acid)

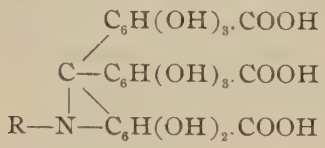


(From Pyrogallol)

Nierenstein considered that these compounds contain a "tannophor" —CO— and formed a hypothesis of the existence of a

[42] Meunier and Seyewetz, *Compt. rend.*, **146**, 987 (1908).
[43] Fahrion, W., See Allen Rogers' Book, "Practical Tanning" (1922), p. 561. Henry Carey Baird & Co., New York.
[44] von Baeyer, *Ber.*, **5**, 25, 280, 1096 (1872).
[45] Caro, *Ibid.*, **25**, 947 (1892).
[46] Kahl, *Ibid.*, **31**, 114 (1898).
[47] Nierenstein, M., *Collegium*, (1905) 221.

tannophor in the tannins. According to the author, the groups designated as "tannophors" are CHO, CO, and CO.O. This supposition was adopted by Stiasny[48] and Kauschke[49] and the latter pointed out that these easily soluble substances exhibit tanning properties. If the formation of leather is viewed in the light of Schiff's base,[50] one may consider the constitutiton of a hexahydroxy-aurinecarboxylic acid leather[51] as follows:



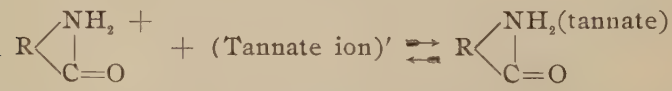
The recent work of Thomas and Foster[52] (1926) on "Behavior of Deaminized Collagen" is another support of the chemical theory of vegetable tanning, and that of Mathur[53] (1927) supports the chemical theory of tanning in the light of oil tannage.

Colloid-Chemical Theory.—The Proctor-Wilson Theory[54] explains the colloidal phenomenon existing between the hide substance and tannin in the tan liquor and when this is followed by Wilson's[55] Chemical Theory, the whole process of tanning is completed in terms colloid-chemical theory. According to Proctor-Wilson theory, when in equilibrium with a tan liquor having a pH value lying in the range 2 to 5, collagen may be looked upon as an aggregate of complex cations balanced by much simpler anions held in the solution immediately in contact with the collagen structure by the same forces that hold all oppositely charged ions together. Under such conditions there exist two electrical potential differences, *i. e.*, the potential difference E between the jelly phase and the external solution, and the potential difference E_1 between the surface film on the tannin particle and the bulk of solution. E

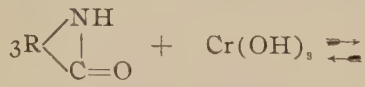
[48] Stiasny, E., *Gerber,* **31**, 233 (1905).
[49] Kauschke, *Collegium,* (1906), 362.
[50] *Ibid.* (1906), 434.
[51] Grasser, G., A book, "Synthetic Tannins," The English translation by Enna, (1922), p. 62-63. Van Nostrand Co., New York.
[52] Thomas, A. W., and Foster, S. B., *J. Amer. Chem. Soc.,* **48**, 489 (1926).
[53] Mathur, B. N., *J. Amer. Leather Chem. Assoc.,* **22**, (1), 2-44 (1927).
[54] Proctor-Wilson Theory, *J. Chem. Soc.,* **109**, 1327, (1916), J. A. Wilson's Book, "The Chemistry of Leather Manufacture" (1923), p. 272-6. The Chemical Catalog Co. New York.
[55] Wilson, J. A., *J. Amer. Leather Chem. Assoc.,* **12**, 108-22 (1917).

and E_1 are of opposite sign. According to the theory, the first important action in the mechanism of tanning results from the tendency for E and E_1 to neutralize each other, and the initial rate of tanning will, therefore, be measured by the sum of the absolute values of the potential differences. Following the Proctor-Wilson theory of the colloidal phenomenon in the tan liquor, Wilson[55] considers a possible chemical combination between the collagen and tannin. The collagen first combines with acid from the liquor, forming an ionizable salt of which the colloid ion is positively charged. If the acid present be represented by HA, then its combination with collagen takes place, thus:

and the subsequent co-precipitation of collagen and tannin as follows:



In case of mineral tannage, Wilson considers alum, chrome and iron leathers as collagen salts of triacid bases:



(Collagen) (Chrome) (Chrome Leather)

Since hide substance consists of aggregates of amino acids in which both amino and carboxyl groups are present, Wilson considers that there are two ways of chemical combination. In case of vegetable tanned leather, the tannin is combined with the amino groups and in case of mineral tanned leather, the metal is combined with the carboxyl groups as represented in the above equations. The colloid-chemical theory of tanning was further discussed by Wilson in an article entitled "Vegetable Tanning as a Colloid-Chemical Process" published in *J. Amer. Leather Chem. Assoc.*, **15**, 374-80 (1920).

Development of the Present Theory

Conception of the Theory.—It has been observed that most of the tanning materials are hydroxy compounds, or condensation products of hydroxy compounds or converted into hydroxy compounds during the tanning operation. Vegetable tannin is a complex form of hydroxy compounds, for upon hydrolysis it yields gallic acid in case of gallotannin and protocatechuic acid in case of catechu-tannin. Synthetic tanning materials are mostly condensation products of hydroxy compounds. The depsides are condensation products of hydroxy benzoic acids. Most of the heat condensation products are obtained from phenolsulfonic acids. The condensation products known as neradols are obtained by coupling phenolsulfonic acids or their derivatives with formaldehyde. Even the non-condensed simple hydroxy compounds have been found to tan. In the British Patents 18,258 and 111,141, a number of simple hydroxy compounds are claimed as tanning agents. The recent work of Mathur[53] on oil tannage has definitely proven that tanning with oil is due to the formation of hydroxy compounds during the tannage. Not only the organic tanning agents are mostly hydroxy compounds, but the mineral tannages are also associated with hydroxy groups. According to Moeller[56] in iron or chromium tanning solutions, alkali is the peptizer and the principal tanning material is the free peptized metal hydroxides. From these facts it may be reasonable to consider the theory that *a hydroxy group or groups in a chemical compound or in a mixture of compounds used for tanning apparently constitute an essential factor in effecting tannage.* As to the mechanism of tanning with certain aromatic hydroxy compounds, the chemical combination theory prevails. However, according to Wilson,[55] there are two ways of chemical combination, *i. e.,* combination of the tanning groups with the amino groups of the hide substance, and combination of the tanning groups with the carboxyl groups of the collagen. In other words, if the tanning material is acid, such as vegetable tannin extract, the acidic groups combine with the amino groups of the hide to form leather. A still more simple term to express this is the process of salt-formation or esterification. Now in the present work, the materials to be tested are mostly aromatic hydroxy compounds, especially naphthol deriva-

[56] Moeller, W., *Z. angew. Chem.*, **35**, 153-4, 160-3 (1922).

tives, in which the hydroxy group has an acid reaction, and therefore it would be more reasonable to assume that the hydroxy groups of the aromatic compounds combine with the basic, amino groups of the collagen. This combination is somewhat different from those assumed by Wilson.[55] Accordingly, if we now represent the hide substance as $R.NH_2$ and the hydroxy compound as $HO.X$, the combination would take place in either of the following two forms:

$$(1) \quad R.NH_2 + HO.X = R.NH.X + H_2O$$
$$(2) \quad R.NH_2 + 2HO.X = R.N.X_2 + 2H_2O$$

In case of reaction (1) only one molecule of the synthetic tannin is absorbed and in case of reaction (2), two molecules, for every amino group in hide.

However, the "hydroxy theory" of tanning must not be overemphasized by assuming that all hydroxy compounds must tan, by virtue of their possible combination with the amino groups of the hide substance, for many hydroxy groups are not active toward tanning, such as alcohol-hydroxy groups. Therefore, it is the purpose of this investigation to find out the types of the hydroxy groups which will cause the compounds to tan, and the criteria which the hydroxy compounds must fulfill before possessing any tanning properties. In order that the work might show an unique feature, the attention was focused on the study of a series of naphthalene derivatives and some other typical compounds. However, the questions concerned would cover various phases of the theory, such as whether all these compounds have tanning properties or whether only some of them show tanning effects, and if so, what are the primary causes for such differences, and above all whether the tannages effected by some of the compounds are really due to the hydroxy groups which constitute the foundation of the present theory.

Recognition of "Leather."—The term "leather" we usually understand to be a piece of hide which has been chemically and physically treated so as to give the desirable technical properties, such as softness, toughness, flexibility and resistibility to hydration and to putrefaction by micro-organisms. However, a defini-

tion of leather is given by Moeller[57] who considers leather as "animal hide of which the elementary parts in the form of submicroscopic intermingled crystal layers are protected from hydrolytic and fermenting influences." Therefore, when a piece of hide is tanned, it will give some, if not all, of the above properties, and if it is not tanned, the hide will remain "raw," *i. e.*, it will swell in water, feel slippery when wet, will be curled or drawn up upon drying and will become transparent, hard, flinty or brittle when dried.

Outline of Work.—The work consisted of a study at first of the gelatine tests so as to detect the glue-precipitating property, if any, of the materials to be used; tanning tests of the materials under different conditions; hide powder analyses for some of the materials which gave tannage; and analyses of some of the leather produced. The greatest attention was paid to the actual tanning experiments, upon which the theory was to be established or rejected.

Behavior of Naphtholsulfonic Acids toward Gelatine Tests.—Since most of the synthetic tanning materials claim to have the property of precipitating glue, gelatine tests were therefore first conducted in order to detect this property in the materials to be used. Accordingly, a 3 per cent gelatine solution was prepared by dissolving a weighed amount of dry, transparent, commercial gelatine in a measured amount of distilled water which was heated to boiling and the heating continued until all the gelatine dissolved. Saturated solutions of various naphtholsulfonic acids were prepared by heating excess of the materials with water above room temperature. When the solution had cooled to room temperature, the gelatine tests were conducted with the various naphtholsulfonic acids, first in acid and then in alkaline solutions.

The naphtholsulfonic acids were then condensed with 37 per cent formaldehyde solution and similar tests made. When a ferric chloride solution was first used to detect the characteristic coloration by the naphtholsulfonic acids, and when the resulting solutions were added with the prepared gelatine, heavy precipitates were obtained, and so other salts, namely aluminum sulphate and

[57] Moeller, W., *Z. angew. Chem.*, **33**, I, 221-3 (1920).

chromium sulphate were subjected to similar tests. The following naphtholsulfonic acids were used:

H-Acid (1-amino-8-naphthol-3:6-disulfonic acid)
Oxy-Laurent's acid (1-naphthol-5-sulfonic acid)
Schaeffer's acid (2-naphthol-6-sulfonic acid)
Gamma acid (2-amino-8-naphthol-6-sulfonic acid)
Nevile and Winther's acid (1-naphthol-4-sulfonic acid)
e-Acid (1-naphthol-3:8-disulfonic acid)
F-Acid (2-naphthol-7-sulfonic acid)
R-Acid (2-naphthol-3:6-disulfonic acid)

Results of the Gelatine Tests

(The gelatine solution was last added in every test)

TABLE I.—Gelatine Tests of the Naphtholsulfonic Acids and Their Formaldehyde Condensation Products.

	+3% Gelatin	+Alkali (NaOH) +3% Gelatin	+Formaldehyde +3% Gelatin
H-Acid	No Ppt.	No Ppt.	Ppt.
Oxy-Laurent's Acid	No Ppt.	No Ppt.	Ppt.
Schaeffer's Acid	No Ppt.	No Ppt.	Ppt.
Gamma Acid	No Ppt.	No Ppt.	Ppt.
Nevile and Winther's Acid	No Ppt.	No Ppt.	No Ppt.
e-Acid	No Ppt.	No Ppt.	Ppt.
F-Acid	No Ppt.	No Ppt.	Ppt.
R-Acid	No Ppt.	No Ppt.	Cloudy

TABLE II.—Precipitation of Gelatine by Mixtures of Naphtholsulfonic Acids and Trivalent Metallic Salts.

	$+FeCl_3$ +3% Gelatin	$+Al_2(SO_4)_3$ +3% Gelatin	$+Cr_2(SO_4)_3$ +3% Gelatin
H-Acid	Ppt.	No Ppt.	No Ppt.
Oxy-Laurent's Acid	Ppt.	Ppt.	Ppt.
Schaeffer's Acid	Ppt.	Ppt.	Cloudy
Gamma Acid	No Ppt.	No Ppt.	No Ppt.
Nevile and Winther's Acid	Ppt.	Ppt.	No Ppt.
e-Acid	Ppt.	No Ppt.	No Ppt.
F-Acid	Ppt.	Ppt.	Cloudy
R-Acid	Ppt.	No Ppt.	No Ppt.

Observations on the Gelatine Tests.—No precipitate was obtained with the gelatine and the naphtholsulfonic acids either in acid or alkaline solution.

Nearly all the condensation products of the naphtholsulfonic acids and formaldehyde gave precipitate with gelatine. These

results are in accord with the claims of various patents[20] on this property.

Nearly all the naphtholsulfonic acids gave a precipitate with gelatine, in the presence of ferric chloride. Aluminum sulphate under the same condition did not act as well. Chromium sulphate yielded a good precipitate only in one case.

Ferric chloride, aluminum sulphate, and chromium sulphate alone did not give any precipitate with the gelatine under the test conditions.

Ferric chloride, aluminum sulphate and chromium sulphate when admixed with the naphtholsulfonic acids in the prepared solutions, did not form any precipitate. The precipitation occurred only when the gelatine solution was added.

The precipitates formed by the presence of ferric chloride were more stable toward dilute HCl than those formed by the presence of aluminum sulphate and chromium sulphate.

The precipitate formed by the gelatine and Oxy-Laurent's acid in the presence of ferric chloride was even insoluble or only difficultly soluble in concentrated HCl.

The precipitates formed in presence of ferric chloride showed characteristic colors, and those formed in presence of aluminum sulphate were usually white, or slightly grey, and those formed in presence of chromium sulphate varied from green to black.

Each datum recorded in the above two tables represents repeated results under both cool and warm conditions.

Discussion on the Gelatine Tests.—Nearly all the commercial synthetic tanning materials precipitate gelatine, and most of the compounds tested by Grasser,[58] which showed tanning effects, also precipitated gelatine. However, the precipitation of gelatine is not a criterion for effecting actual tannage with raw hides. In 1907 Stiasny[59] found that maclurin precipitated gelatine but had no tanning effect on the raw hide. Grasser[58] also concluded that tannoid properties of different synthetic tanning materials are not dependent on whether they precipitate gelatine or are absorbed by hide powder or not. Hydroxynaphthylmethanesulfonic acid, for instance, precipitates gelatine but does not convert pelt into leather;

[58] Grasser, G., A book, "Synthetic Tannins," The English translation by Enna (1922), p. 66; 68. Van Nostrand Co., New York.

[59] Stiasny, E., *Gerber*, **788**, 185 (1907).

on the other hand, sodium dicresylmethanesulfonate does not precipitate gelatine, and neither does it tan pelt; nevertheless it is absorbed by hide powder as "tanning matter;" o-nitrophenol does not precipitate gelatine, but has some tanning action on both hide powder and pelt.

In the present tests although none of the naphtholsulfonic acids was found to precipitate gelatine, they might have tanning properties, and therefore actual tanning experiments had to be conducted before a final conclusion on their tanning properties was drawn.

The precipitation of the gelatine by the condensation products of the naphtholsulfonic acids and formaldehyde is an expected property as has been shown by various investigators.

The discovery of the precipitation of the gelatine by the naphtholsulfonic acids in presence of the trivalent metallic salts, especially ferric chloride, warranted further investigation and study. Since the naphtholsulfonic acids alone, or the metallic salts alone, did not form any precipitate with the gelatine under the test conditions, but their admixtures formed heavy precipitates, the metallic salts must play some peculiar part in the precipitation. Although colloid chemistry shows that these salts are powerful precipitants of colloidal sols, they do not apply to the gelatine which is the best protective colloid, and it was a fact that these salts alone did not precipitate gelatine even on repeated tests. However, the fact itself suggested that possible tannages might be effected by the combinations of these naphtholsulfonic acids and the metallic salts, especially ferric chloride. Full explanations of this phenomenon will be seen later.

Behavior of Naphthalene Derivatives as Tanning Agents.— Since the discovery of the neradols by Stiasny[60] in 1911, many investigators have experimented on formaldehyde condensation products, and have succeeded in making new synthetic tanning materials in this way. These researches extend to naphthalene derivatives. The Deutsche Koloniale Gerb- and Farbstoff-Ges,[61] Karlsruhe, Germany, was the most far-sighted in this direction.

[60] Stiasny, E., Ger. Pat. 262,558 (1911); *J. Soc. Chem. Ind.*, **32**, 775-7 (1913).
[61] Deutsch Koloniale Gerb. and Farbstoff-Ges., Ger. Pat. 293,042; 293,640; 293,693; 303,640. Brit. Pat. 8,818; 18,174.

Immediately following the suggestion by Stiasny in 1911, this Company started to manufacture synthetic tanning materials from condensation products of formaldehyde and naphtholsulfonic or aminonaphtholsulfonic acids and their processes are now protected by both German and British Patents. By using a different process, A. Römer[62] also obtained a U. S. Patent to manufacture condensation products of formaldehyde and naphtholsulfonic or aminonaphtholsulfonic acids, as tanning agents. O Schmidt[63] obtained a number of U. S. Patents by using formaldehyde and naphthalenesulfonic acids, which are free from naphthol groups. Differentiating from the process of O. Schmidt, Badische[64] used heat or phosphorus pentachloride condensation products of naphthalenesulfonic acids which are not only free from naphthol groups but from the intervention of formaldehyde. F. Hassler[65] claimed a process of manufacturing condensation products from naphthalene-sulfonic acids which are free from both (CH_2) and (OH) groups; the condensing agent being merely heat. However, by using suitable condensing agents, naphthalenesulfonic acids are easily condensed and so in the process of Chemische Fabriken Worms Akt.-Ges,[66] phosphorus pentachloride or sulphur chloride are used, and in that of A. Römer,[67] phosphorus oxychloride, as condensing agents. All of these synthetic tanning agents are condensation products from naphthalene derivatives, and the various investigators seem to be of the opinion that condensation products are the best tanning agents, because they have larger molecules. On the other hand very little is known or published on simple naphthalene derivatives for tanning purposes. In the present research, the simple naphthalene derivatives were used for tanning experiments, which is a feature of marked difference from previous investigations.

With the importance of the "Hydroxy Theory" in mind, naphthol-sulfonic acids were first taken for study, because in these compounds, there is not only a hydroxy group in forming the naphthol, but also a hydroxy group present in the sulfonic radical.

[62] A. Römer, U. S. Pat. 1,186,500.
[63] O. Schmidt, U. S. Pat. 1,191,480; 1,216,612; 1,278,229; 1,336,759. Canad. Pat. 228,241.
[64] Badische, Brit. Pat. 17,172.
[65] F. Hassler, U. S. Pat. 1,501,336; 1,533,594.
[66] Chemische Fabriken Worms Akt.-Ges., Brit. Pat. 148,126.
[67] A. Römer, U. S. Pat. 1,375,975.

This procedure seemed to be a proper method of attack on the hydroxy theory.

Drum Tanning Experiments.

The preliminary tanning experiments were conducted in rotating 1-quart glass jars. Each jar was provided with a rubber gasket and a screw top. The jars were held tight in a wooden box having 4 compartments. The system was connected to an electric motor, causing it to rotate at the rate of about 20 R.P.M.

The skins used throughout all the experiments were sheep fleshers. The skins as received from their manufacturer had been regularly bated and pickled, and were kept in a moist condition. In preparing the tanning pieces, a full skin was cut into uniform sizes of 5″ x 6″. Two such pieces weighing totally about 25 grams were used for each tanning liquor.

In the tanning process, the skins were put into the bottles and then the prepared tanning liquors added. The bottles were closed water-tight and then put into the rotating machine. After running for a sufficient time the skins were removed and without washing hung up to dry over night. The next day, when the skins had become dried or nearly so, they were washed in plain water in the rotating bottles, and after being thoroughly washed were pressed on a setting table to remove the excess of water, and were then dried again at the room temperature. When thoroughly dried they were carefully examined and the tannages were graded according to the following specifications.

"Tan A" means that the skins after the treatment with the tanning liquor showed no curls, became very soft on slight pulling, were entirely opaque, uniformly and thoroughly penetrated by the tanning material, and possessed good tensile strength.

"Tan B" means that the skins after the treatment with the tanning liquor showed no curls, became very soft or only slightly hard, were opaque or semi-opaque, thoroughly penetrated by the tanning material, and possessed good tensile strength.

"Some Tan" means that the skins after the treatment with the tanning liquor showed some but not much curls, became hard but not flinty, were semi-opaque but not transparent, partly but not thoroughly penetrated by the tanning material, tough but not brittle.

"No Tan" means that the skins after the treatment with the tanning liquor still appeared as raw hide, or were much curled up by drying, felt papery or flinty, were little penetrated or not penetrated at all by the tanning material, might be tough or brittle, or cracky at the surface.

"Plus or Minus Marks" means better or worse qualities of the same grade, being based on the judgment at the time of examination.

Experiment 1. *Tanning with Excess of Dilute Solutions.*—The following naphtholsulfonic acids were used:

H-Acid (1-amino-8-naphthol-3:6-disulfonic acid)
Oxy-Laurent's acid (1-naphthol-5-sulfonic acid)
Schaeffer's acid (2-naphthol-6-sulfonic acid)
Gamma Acid (2-amino-8-naphthol-6-sulfonic acid)
Nevile and Winther's acid (1-naphthol-4-sulfonic acid)
e-Acid (1-naphthol-3:8-disulfonic acid)
F-Acid (2-naphthol-7-sulfonic acid)
R-Acid (2-naphthol-3:6-disulfonic acid)

Ten grams of each acid was dissolved in 500 cc. of water contained in the 1-quart jar, and then two pieces of the cut-skin were added. The bottles with their contents were closed and put into the rotating machine and run for two hours. They were taken out and hung to dry overnight. On the next day they were washed in the drum with water for half an hour, and then pressed on the setting table and dried in air.

RESULTS OF EXPERIMENT 1.

Name of Material	Tannage	Color	Special Remarks
H-Acid	Some Tan	Chocolate	Penetrated
Oxy-Laurent's Acid	No Tan	Black	Only surface tanned
Schaeffer's Acid	No Tan	Colorless	Still raw hide
Gamma Acid	Some Tan	Brown	Partly penetrated
Nevile & Winther's Acid	Some Tan	Pink	Penetrated
e-Acid	No Tan	Chocolate	Gelatinized
F-Acid	No Tan	Black	Only surface colored
R-Acid	No Tan	Colorless	Still raw hide

OBSERVATIONS

Little tannages were obtained in this experiment perhaps because the solutions were too dilute, and the time was too short. The skins after tanning came out rather hard, curled, or transparent.

Experiment 2. Tanning with 5 per cent Material in Just Enough Liquor.—Five per cent of each of the above mentioned naphtholsulfonic acids, based on the weight of the moist skin, *e. g.*, 1.25 grams of acid to 25 grams of skin, was dissolved or suspended in 50 cc. water. In cases of H-acid, Schaeffer's acid, Gamma acid and R-acid, such amounts of acid were not completely soluble in 50 cc. water and therefore partly held in suspension. Two pieces of the cut-skin were used for each tanning liquor. The drumming was run for one hour, and then the skins were taken out and hung to dry overnight. On the next day they were washed in plain water for half an hour, pressed and dried as before.

RESULTS OF EXPERIMENT 2.

Name of Material	Tannage	Color	Special Remarks
H-Acid	Some Tan	Chocolate	Penetrated
Oxy-Laurent's Acid	Some Tan	Blue-black	Flat, penetrated
Schaeffer's Acid	No Tan	Colorless	Curled, transparent
Gamma Acid	Tan B	Grey-brown	Soft, thoro penetrated
Nevile & Winther's Acid	Tan B	Pink	Soft but little curled
e-Acid	Some Tan	Chocolate	Penetrated but hard
F-Acid	No Tan	Black	Only surface colored
R-Acid	No Tan	Colorless	Curled, transparent

OBSERVATIONS

After tanning nearly all the tan liquors were taken up by the skins and after washing and drying, more tannages were obtained than from the previous experiment. This method of tanning, *i. e.*, by using just enough tan liquors seemed to be more promising, and therefore subsequent experiments were made following this method.

Experiment 3. Successive Tannings with 5 Per Cent Material. This was a repetition of Experiment 2, except that after the first tanning and before washing with water, the skins were tanned a second time and then one piece from each pair of skin was washed and dried, and the other pieces were tanned a third time, and then washed and dried, the idea being to see whether successive tanning and drying would improve the tannage or not.

RESULTS OF EXPERIMENT 3-A. TWO TANNINGS.

	Tannage	Color	Special Remarks
H-Acid	Tan B	Chocolate	Thoro penetrated
Oxy-Laurent's Acid	Tan B	Blue-black	Full but slightly hard
Schaeffer's Acid	No Tan	Colorless	Curled, transparent
Gamma Acid	Tan A	Dark-grey	Very soft and full
Nevile & Winther's Acid	Tan A	Pink	Soft and full
e-Acid	Tan B	Chocolate	Thoro penetrated
F-Acid	No Tan	Black	Only surface colored
R-Acid	No Tan	Colorless	Transparent and curled

RESULTS OF EXPERIMENT 3-B. THREE TANNINGS.

H-Acid	Tan B—	Chocolate	Thoro penetrated but hard
Oxy-Laurent's Acid	Tan B	Blue-black	Full but hard
Schaeffer's Acid	No Tan	Colorless	Curled, transparent
Gamma Acid	Tan A	Dark-grey	Very soft and full
Nevile & Winther's Acid	Tan A—	Pink-red	Full but not so soft
e-Acid	Tan B—	Chocolate	Full but harder
F-Acid	No Tan	Black	Some penetration
R-Acid	No Tan	Colorless	Transparent and curled

OBSERVATIONS

Third tanning did not improve the qualities of the skins from second tanning, and in some cases it made the skin feel harder, though the penetration from third tanning was fuller.

Experiment 4. Tanning with 10 Per Cent Material.—This tanning was conducted in a similar way as in the previous experiments, except that 10 per cent of the material was used and the drumming was carried for three hours. The skins were hung to dry overnight and then washed as before.

RESULTS OF EXPERIMENT 4. TEN PER CENT MATERIAL AND 3-HOUR DRUMMING.

	Tannage	Color	Special Remarks
H-Acid	Tan B	Chocolate	Thoro penetrated
Oxy-Laurent's Acid	Tan A—	Blue-black	Full and fairly soft
Schaeffer's Acid	No Tan	Colorless	Semi-transparent
Gamma Acid	Tan A	Dark-grey	Very soft and full
Nevile & Winther's Acid	Tan A	Pink	Soft and full
e-Acid	Tan B	Chocolate	But slightly hard
F-Acid	No Tan	Black	Some penetration
R-Acid	No Tan	Colorless	Transparent and hard

OBSERVATIONS

Tannages produced from this experiment were better than those from previous experiments. It raised the qualities of those skins

which were tanned, but it did not change the qualities of those skins which did not react with the other materials.

Experiment 5. Tanning with Excessive Materials.—Excessive materials were suspended in just enough liquors, and in cases of H acid, Schaeffer's acid, gamma acid, and R-acid, these liquors appeared as thick pastes, due to their small solubility, and in cases of Oxy-Laurent's acid, Nevile and Winther's acid, e-acid, and F-acid, the liquors were in form of suspension, because they were considerably soluble. The drumming was run for three hours. After tanning the skins were hung to dry overnight, and then washed and dried.

Results of Experiment 5. Excessive Materials.

	Tannage	Special Remarks
H-Acid	Tan B	Fully penetrated but rather hard
Oxy-Laurent's Acid	Spoiled	All curled up, and brittle
Schaeffer's Acid	No Tan	Still transparent and hard
Gamma Acid	Tan A	Very soft but greasy
Nevile & Winther's Acid	Spoiled	All curled up and brittle
e-Acid	Tan B—	Fully penetrated but rather hard
F-Acid	No Tan	Only surface colored
R-Acid	No Tan	Still transparent and hard

Observations

In general, excessive materials did not give so good tannages as obtained from experiment 4 with 10 per cent material. Still worse result was that excessive Oxy-Laurent's acid and Nevile and Winther's acid caused the skins to contract and curl, and when these dried, they broke like pieces of wood, although the skins were fully penetrated. However, this showed definite actions of these two acids on the skin and suggested that if these two acids are used at proper concentrations, good tannages may be obtained. Those acids which did not show any tanning effects in previous experiments still remained so in this experiment.

Experiment 6. Tanning with 10 Per Cent Materials in Form of Sodium Salts.—A 10 per cent material based on weight of the skin was used in each case. The material was first made alkaline with NaOH solution and then brought back to acid with acetic acid. Just enough liquor was used, so that after tanning, the liquor would be all taken up by the skin. The drumming was

run for three hours. The skins were hung to dry overnight and then washed and dried.

RESULTS OF EXPERIMENT 6. TEN PER CENT MATERIALS AS SODIUM SALTS.

	Tannage	Color	Special Remarks
H-Acid	Tan A—	Brown	Soft and firm
Oxy-Laurent's Acid	Tan A—	Blue-black	Soft and firm
Schaeffer's Acid	No Tan	Colorless	Transparent
Gamma Acid	Tan A+	Grey	Very soft and full
Nevile & Winther's Acid	Tan A	Pink-red	Soft and firm
e-Acid	Tan B	Brown	Full but hard
F-Acid	No Tan	Black	Only surface colored
R-Acid	No Tan	Colorless	Transparent and hard

OBSERVATIONS

Tannages produced from this experiment were still better than those from experiment 4. These two experiments used the same amounts of materials and the same length of time, but in experiment 4, the materials used were direct acids among which H-acid, Schaeffer's acid, Gamma acid and R-acid were only slightly soluble, while in form of their sodium salts, as used in this experiment, they were rendered completely soluble, therefore H-acid and Gamma acid gave comparatively better tannages. It should be noted here that Gamma acid thus far stood out as the best tanning agent, and those which did not show tanning effects as acids still remain tanning-inactive as sodium salts.

Experiment 7. Tanning with 30 Per Cent Materials in Form of Sodium Salts.—This was a repetition of Experiment 6, except that in this experiment 30 per cent materials were used. The solutions were made in the same way and reacted only slightly acid. The time of drumming was also three hours.

RESULTS OF EXPERIMENT 7. THIRTY PER CENT MATERIALS AS SODIUM SALTS.

	Tannage	Special Remarks
H-Acid	Tan A—	Very soft but very greasy
Oxy-Laurent's Acid	Tan B	Full but slightly greasy
Schaeffer's Acid	No Tan	Hard and semi-transparent
Gamma Acid	Tan A+	Very soft but very greasy
Nevile & Winther's Acid	Tan A—	Soft but slightly greasy
e-Acid	Tan A—	Soft but very greasy
F-Acid	No Tan	Some penetration
R-Acid	No Tan	Still transparent and hard

Observations

All those which showed tanning effects gave softer leathers at such higher concentrations, but the leathers produced were very greasy due to apparent polymerization. Such greasy feeling was not removed by washing either with sodium carbonate or with soap. However, it was afterwards removed by washing with naphtha, and after this treatment the leathers produced felt soft, dry and porous. The grades recorded above were after water wash and before naphtha treatment. Another peculiar thing from this experiment was that there was a kind of substance formed from the tanning material and the hide, which was especially noted on the surface of the skin and which was removable by scratching with a blade. Such substance was formed only by those which gave tannage.

Experiment 8. Influence of Concentration on Tanning Effects. —Those materials which showed promising tanning properties were determined quantitatively at different concentrations for their optimum tanning reactions. Accordingly 5 per cent, 10 per cent, 15 per cent and 20 per cent of the materials based on the weight of raw skin were dissolved or suspended in just enough water and neutralized with NaOH solution till just alkaline, and then brought back to acid condition by a little acetic acid. In this way all the materials used were rendered completely soluble in water. The drumming was carried for three hours, and then the skins were taken out and hung to dry overnight, washed and dried.

Results of Experiment 8. Influence of Concentration.

	5%	10%	15%	20%
H-Acid	Tan B—	Tan A	Tan B	Tan B—
Gamma Acid	Tan B—	Tan A+	Tan A+	Tan A
Nevile & Winther's Acid	Tan B—	Tan A	Tan A+	Tan B
e-Acid	Some Tan	Tan B	Tan B	Tan B—

Observations

It is found here that proper quantities of materials to be used lie between 10 and 15 per cent based on the weight of the hide. Gamma acid as sodium salt has a wider range of concentrations in which this material can yield good tannage. However, such tan-

nages will also depend on time and kind of skin to be used.

Experiment 9. Tanning by Immersion in Dilute Solutions.—Twenty grams of each material was dissolved or suspended in 500 cc. of water and made alkaline with NaOH and then brought back to acid with acetic acid. Two pieces of the prepared cut skins were immersed in the solution. The bottles with their contents were drummed for three hours and then let to stand for 24 hours. The skins were washed and dried.

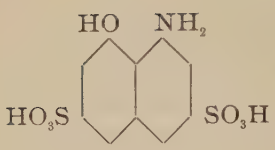
RESULTS OF EXPERIMENT 9. TANNING BY IMMERSION IN DILUTE SOLUTIONS.

	Tannage	Special Remarks
H-Acid	Some Tan	Thoroly penetrated, but hard
Gamma Acid	Tan A	Soft and full but greasy
Nevile & Winther's Acid	Tan A+	Soft, and nearly white
e-Acid	Some Tan	Thoroly penetrated, but hard

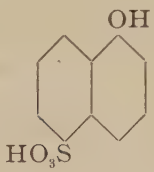
OBSERVATIONS

In drum-tanning with just enough concentrated solutions, Gamma acid gave the best tannage, but in case of vat-tanning with dilute solutions Nevile and Winther's acid gave the best tannage. H-acid yielded a somewhat gelatinized skin, and e-acid, a still more gelatinized one, however, the skins were thoroughly penetrated by the materials and not much curled upon drying, and appeared opaque to light, though they felt rather hard. It seemed that vat-tanning was not so efficient as drum-tanning especially for these naphthol sulfonic acids.

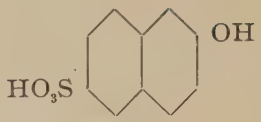
First Observation of the Hydroxy Theory.—In the above experiments it was found that some naphtholsulfonic acids showed definite tanning effects, while others did not show tanning effects at all, and those which did not show tanning effects in the first two experiments remained inactive in subsequent tests. No matter whether they were used in dilute or in concentrated solutions or even in form of pastes, such materials both as acids and as salts remained tanning-inactive and the skins treated by them turned out curled, hard and transparent and in some cases very raw. In order to afford some sort of explanation for such difference, the structural formulae of these materials were first studied.



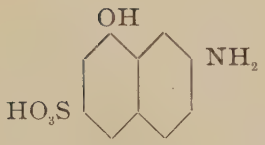
H-Acid
(Tan)



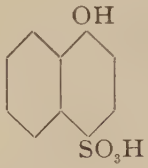
Oxy-Laurent's
Acid
(Tan)



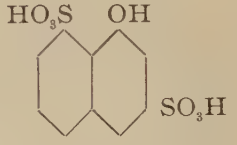
Schaeffer's
Acid
(No Tan)



Gamma Acid
(Tan)



N & W Acid
(Tan)



e Acid
(Tan)

F-Acid
(No Tan)

R-Acid
(No Tan)

Here it was noticed that all those marked "Tan" have the hydroxy (OH) group on the alpha position of the naphthalene rings, and all those marked "No Tan" have the hydroxy (OH) group on the beta position. Their sulfonic (SO_3H) groups may have the same positions such as in the case of Gamma acid and Schaeffer's acid and also in the case of H-acid and R-acid, but these compounds do not show the same tanning effects, and the reason must be due to the difference in position of the (OH) group. If one should argue by the reason that in H-acid and Gamma acid each has one additional amino group and therefore its tanning effect is different from that of Schaeffer's acid, or R-acid, the answer would be that amino group is not the primary tanning group, for in the case of Oxy-Laurent's acid and Nevile and Winther's acid, both have no amino group but tan just the same.

Now in considering the sulfonic groups, we will notice that both alpha and beta naphtholsulfonic acids have in common sulfonic groups, but beta-naphtholsulfonic acids do not tan while alpha-naphtholsulfonic acids do, the sulfonic groups, evidently, are not the primary tanning groups. From this fact, it can be easily seen that the hydroxy (OH) group in the sulfonic radical is quite different from the hydroxy group directly attached to naphthalene rings. Further proofs on the difference of these two kinds of hydroxy groups can be shown by qualitative tests with ferric chloride, the (OH) group directly attached to the naphthalene rings giving characteristic color reactions, while the (OH) group in sulfonic radical producing no color change. These are known facts and need no demonstration.

Having eliminated both amino and sulfonic groups as primary tanning groups, we now only need to consider the hydroxy group directly attached to the naphthalene rings. By further study of the positions of such (OH) groups, it will be noted that the tanning effects of the naphthol derivatives depend on alpha position of the naphthol group only and not on any one of the alpha positions, 1, 4, 5, or 8, because the alpha-naphtholsulfonic acids having their (OH) group at different positions all show tanning effects.

Comparison of the Tanning Effects of Alpha and Beta Naphthols.—Since a fundamental principle had been developed to the point that the alpha-naphthol group is the primary tanning group of the naphthalene derivatives, it was thought that tanning experiments with pure naphthols free from other groups, would help show the truth or fallacy of this hypothesis. Accordingly, such experiments were accurately conducted as follows:

Experiment 10. Tanning with Alpha and Beta Naphthols in Alcohol.—Since both alpha and beta naphthols are very insoluble in water, no attempts were made to use their water-solutions for tanning. However, these two naphthols are known to be very soluble in alcohol, so their alcoholic solutions were subjected to tanning experiments, knowing that the solvent would not influence the tannage.

	Materials for Alpha-Naphthol	Materials for Beta-Naphthol
Weight of 2 pieces of skin	20 grams	22 grams
Weight of a- or b-Naphthol	10 grams	11 grams
cc. 95 per cent denatured alcohol	100 cc.	100 cc.

The drum-tanning with these mixtures was carried for 4 hours, and the skins were taken out and hung to dry overnight. The next day the skins were washed in plain water for 1 hour and pressed and dried in air.

RESULTS OF EXPERIMENT 10. a- AND b-NAPHTHOLS IN ALCOHOL.

Description of Skins	Skins from Alpha-Naphthol	Skins from Beta-Naphthol
Tanning	Tan B	No Tan
Curling	No Curl	Much Curl
Feeling	Soft	Papery
Transparency	Opaque	*Uncertain
Greasiness	Non-greasy	Non-greasy
Penetration	Thorough	*Uncertain
Coloration	Pinkish	Whitish

OBSERVATIONS

The results recorded above were those from a third experiment with the naphthols. In the first experiment, the materials used were not measured and the results were in accord with the present results. In the second experiment, 100 per cent naphthols based on the weights of the hide were used, but after drumming the skins were curled and contracted to small sizes and thus spoiled. So in the third experiment only 50 per cent materials were used and the tanning was successful without curling up the skins. After washed with plain water and dried in air, those skins treated by alpha-naphthol showed no curling, felt soft, and were thoroughly penetrated, and in general had the appearance of a leather tanned by alpha-naphtholsulfonic acid-1:4. The skins treated by beta-naphthol were curled and felt hard or papery. The outside surface was deposited with a coat of beta-naphthol and so its opaqueness might be due to this coating, and for the same reason its penetration could not be definitely identified, and therefore, these properties were recorded as "uncertain."* However, the skins treated by beta-naphthol were untanned, judging from the general appearance and feel of leather. On the other hand, the skins treated by alpha-naphthol did not have such a coat of the naphthol and their leathery properties could be easily recognized.

Experiment 11. Tanning with a- and b-Naphthols in Alkaline Solutions.—It is also known that these two naphthols were very soluble in concentrated alkalies, but on the other hand, concen-

trated alkalies are powerful plumping and gelatinizing agents which always swell and curl the skins. Therefore a scheme was evolved to compensate these factors by using a small amount of alkali and much excess of the naphthols, so that the presence of the little alkali would bring an infinitesimal amount of the naphthols into solution to react with the skins constantly in the drumming process.

	Materials for Alpha-Naphthol	Materials for Beta-Naphthol
Weight of 2 pieces of skin	20 grams	19 grams
Weight of a- or b-Naphthol	20 grams	19 grams
cc. ½ N NaOH solution	10 cc.	10 cc.
cc. distilled water	100 cc.	100 cc.

The drumming with these mixtures was carried for 4 hours and the skins were taken out and hung to dry overnight and then washed and dried.

RESULTS OF EXPERIMENT II. a- AND b-NAPHTHOLS IN ALKALINE SOLUTIONS.

Description of Skins	Skins from Alpha-Naphthol	Skins from Beta-Naphthol
Tanning	Tan A	No Tan
Curling	No Curl	Much Curl
Feeling	Very soft	Hard and papery
Transparency	Opaque	Opaque
Greasiness	Non-greasy	Non-greasy
Penetration	Penetrated	Penetrated
Coloration	Pinkish	Whitish

OBSERVATIONS

The leather turned out by alpha-naphthol was still better than that from previous experiment and very similar to that tanned by alpha-naphtholsulfonic acid-1:4. Beta-naphthol still remained tanning-inactive.

Discussion of the Tanning Effects of alpha- and beta-Naphthols.—In the experiment with alcoholic solutions, no other impurities except the tanning-inactive alcohol were introduced, therefore, any tanning effects produced will be entirely due to the naphthols alone, and since there are no other groups except the (OH) group present in the naphthalene rings, the tanning effects produced cannot be attributed otherwise but to (OH) group directly attached to the naphthalene rings. Since alpha-naphthol has definite tanning

effects, while beta-naphthol has no sign of the capacity to tan, the only reason that can account for this difference is the position of the (OH) group in the naphthalene rings, therefore the hypothesis, that the tanning properties of naphthalene derivatives, at least for naphtholsulfonic acids, are dependent only on the (OH) group in the alpha position of the naphthalene rings, is apparently valid, as far as experiments go. The tanning with the naphthols in the alkaline solutions showed a much better contrast in which alpha-naphthol yielded a leather which is even better than that yielded by some of the alpha-naphtholsulfonic acids, while beta-naphthol, on the other hand, did not show any tanning effects at all. If one does not hold that NaOH is the influencing agent, this is another support of the hypothesis. From these two experiments we can now trace back and explain the differences in the tanning effects existing in the naphtholsulfonic acids as tested above, because these naphtholsulfonic acids are made directly or indirectly from the simple naphthols as their mother substances.

However, there is considerable controversy over the tanning properties of a- and b-naphthols in the literature. In 1907, Weinschenk[68] claimed a process of using a- and b-naphthols in conjunction with an aldehyde as tanning agents. Since the controversies are based on this patent, the text[69] of its specification is here first given: "Although the naphthols are only weak tanning agents per se, but they may advantageously be used if the hides are first prepared with an aldehyde. Aldehydes of the aliphatic and aromatic series, such as formaldehyde, acetaldehyde, resorcylaldehyde, pyrogallolaldehyde, may be used. The hides may be also first saturated with naphthol, and then (in the presence of an additional quantity of the reagent) treated with the aldehyde; or the naphthol and aldehyde may be made into a paste with water and gradually added to the prepared hides, suspended in water at 30°-35° C. and kept moving."

After Weinschenk had published his results[70] on tanning with the naphthols, Stiasny[71] was the first to attack his work by saying that the formation of a tanning agent by the use of naphthol

[68] Weinschenk, A., English Patent 4605, Feb. 25, 1907.
[69] *J. Soc. Chem. Ind.*, **26**, 1100, (1907).
[70] *Chem. Ztg.*, **31**, 549 (1907).
[71] *Ibid.*, **32**, 509 (1908).

and formaldehyde is a failure, and conducted experiments[72] to show the fallacy of Weinschenk's conclusions with reference to a- and b-naphthol solutions as tanning agents. Ricevuto and Nierenstein[71] supported Stiasny and Nierenstein even went so far as to say that tanning with the naphthols is "theoretically as well as practically impossible."

In replying to these charges, Weinschenk[73] conducted experiments to show that naphthols actually combine with gelatine in the presence of formaldehyde, and found that gelatine, when first treated with formaldehyde, was precipitated by the subsequent addition of a- or b-naphthol. Formaldehyde alone did not give such a precipitate.

However, Stiasny[74] rebutted his opponent by saying that the gelatine reaction does not necessarily prove that these substances actually tan, as for example, maclurin is precipitated by gelatine but has no tanning effect. The author particularly emphasized that b-naphthol alone or in connection with formaldehyde does not tan nor has it any action whatsoever, and that the sole action is due to the formaldehyde alone.

The present investigation, especially in the last two experiments, throws much light on this argument. In general, both sides are partly right. Weinschenk is right by noticing that alpha-naphthol has tanning effects, but partly wrong by saying that both a- and b-naphthols are weak tanning agents, and still better tanning agents in connection with an aldehyde. Stiasny is right by emphasizing that b-naphthol has neither tanning effects nor any action on the skin, but partly wrong in saying that tanning with the naphthols is a complete failure, having not realized that alpha-naphthol alone when used in alcoholic solution and in dilute alkaline solution turned out good leather. Nierenstein is entirely ungrounded by saying that tanning with the naphthols is "theoretically impossible."

Criterion of Alpha-Naphthol and Further Proofs of the Theory.—The above experiments especially those with pure naphthols have brought to light the fact that alpha-naphthol is the criterion for the tanning properties of all simple naphthol derivatives. It

[72] *Ibid.*, **32**, 383, 586 (1908).
[73] Weinschenk, A., *J. Soc. Chem. Ind.*, **27**, 347 (1908).
[74] Stiasny, E., *Gerber*, **788**, 185 (1907).

would be of prime importance to test all other alpha-naphthol as well as beta-naphthol derivatives for their tanning properties, before this criterion could be of any value. Accordingly, all the naphthol derivatives based on the "Census of Dyes and Other Synthetic Organic Chemicals,[75] 1925" were obtained for these experiments. An effort was made to get all of these compounds, and only a few, however, could not be secured.

Since drum-tanning had proven more efficient than the vat-tanning process for these compounds, the former was followed in the subsequent experiments. Since from 10 per cent to 15 per cent of the material had been found to be the most satisfactory quantities for these tests, 15 per cent was used for the sake of safety. The drum was run for three hours, and after tanning the skins were hung to dry. They were then washed in plain water, pressed free from excess of water, and again dried.

In the first instance, the acids as received were used. Then the corresponding sodium salts were prepared by first making the solution slightly alkaline and bringing it back to acid condition by means of acetic acid.

The following are the results of various experiments conducted according to the above:

Experiment 12. Tanning with Alpha-Naphthol Derivatives as Acids.—The following a-naphtholsulfonic acids or their derivatives were used:

S-acid—(1-amino-8-naphthol-4-sulfonic acid)
J-acid—(2-amino-5-naphthol-7-sulfonic aicd)
Chicago acid—(1-amino-8-naphthol-2:4-disulfonic acid)
Phenyl-gamma acid—(phenyl-2-amino-8-naphthol-6-sulfonic acid)
Phenyl-J-acid—(phenyl-2-amino-5-naphthol-7-sulfonic acid)
Chloro-H-acid—(1-naphthol-8-chloro-3:6-disulfonic acid)
Chromotropic acid—(1:8-dihydroxynaphthalene-3:6-disulfonic acid)
1:5-dihydroxynaphthalene
I-acid Imid.—(2:2-dinaphthylamino-5:5-dihydroxy-7:7-disulfonic acid)
From National Aniline & Chemical Co.
Rhoduline Acid—(5:5-dihydroxy-7:7-disulfonic-2:2-dinaphthylamine)
From DuPont de Nemours & Co.
J-acid Urea—(5:5-dihydroxy-7:7-disulfonic-2:2-dinaphthyl urea)
From DuPont de Nemours & Co.

[75] Census of Dyes and Other Synthetic Organic Chemicals, (1925), p. 27-32. Tariff Information Series No. 34. Published by U. S. Tariff Commission, Washington. Obtained from Washington Government Printing Office.

RESULTS OF EXPERIMENT 12. TANNING WITH ALPHA-NAPHTHOL DERIVATIVES AS ACIDS.

	Tannage	Color	Special Remarks
S-acid	Tan A	Black	Very soft, inside grey
J-acid	Tan B	Dark-brown	Penetrated, slightly hard
Chicago acid	Tan A+	Green	Very soft and full
Phenyl-gamma acid	Tan A	Dark-grey	Soft and full
Phenyl-J-acid	Tan B—	Dark-grey	Slightly hard
Chloro-H-acid	Some Tan	Grey-brown	Flat, semi-opaque
Chromotropic acid	No Tan	Dark-green	Penetrated but hard
1:5-Dihydroxynaphthalene	No Tan	Light-grey	Semi-opaque and hard
I-acid Imid	Tan A	Dark-grey	Soft and full
Rhoduline acid	Tan A+	Green-brown	Very soft and full
J-acid urea	Tan A+	Pink-grey	Very soft and full

OBSERVATIONS

All of the alpha-naphthol derivatives except three, gave rather good tannages, and the leathers produced by them were very soft, opaque and fully penetrated. There were three which did not show up so well, but even these gave a satisfactory tannage under special conditions which will be mentioned later.

Experiment 13. Tanning with Alpha-Naphthol Derivatives as Sodium Salts.—

The same materials listed under Experiment 12 were used. The materials (15 per cent on weight of the hide) were made alkaline with NaOH, and then brought back to an acid condition with acetic acid. The drum was run for three hours and the skins hung to dry. They were finally washed in plain water, pressed and dried.

RESULTS OF EXPERIMENT 13. TANNING WITH a-NAPHTHOL DERIVATIVES AS SODIUM SALTS.

	Tannage	Color	Special Remarks
S-acid	Tan A	Black	Very soft, inside grey
J-acid	Tan B+	Dark-brown	Only slightly hard
Chicago acid	Tan A+	Dark-green	Very soft and full
Phenyl-gamma acid	Tan A	Dark-grey	Soft and full
Phenyl-J-acid	Tan A+	Green-brown	Very soft and full
Chloro-H-acid	Some Tan	Grey-brown	No curl but hard
Chromotropic acid	No Tan	Dark-green	Penetrated but hard
1:5-Dihydroxynaphthalene	No Tan	Light-grey	Semi-opaque and hard
I-acid Imid	Tan A+	Dark-grey	Very soft and full
Rhoduline acid	Tan A+	Blue-brown	Very soft and full
J-acid urea	Tan A+	Chocolate	Very soft and full

OBSERVATIONS

The sodium salt in no case diminished the tanning property of the corresponding acid, but in most cases improved it. Chloro-H-

acid and Chromotropic acid, which did not tan as acids, act in the same manner as salts. These two acids showed remarkable penetration, but as the skins became hard and slightly curled upon drying, they were considered as "No Tan" in spite of their thorough penetration. These materials showed tanning properties by special treatments as will be shown in the following experiments:

Experiment 14. Special Tanning with Chloro-H-Acid.—Since chloro-H-acid differs from H-acid only in one respect, *i. e.*, in chloro-H-acid the amino (NH_2) group of H-acid has been substituted by Cl, it was thought that by using the ammonium salt of chloro-H-acid the NH_4 group introduced might act as the NH_2 group. This time, a 30 per cent chloro-H-acid was used and made alkaline with NH_4OH and then brought back to acid with HCl. The tanning was conducted for three hours, the skins were hung to dry, then washed and dried again as usual. The dried skins, after such treatments, were very soft, opaque, and had the good feel of regular leather.

Experiment 15. Special Tanning with Chromotropic Acid.—The above scheme of using the ammonium salt was tried, but it failed in the case of chromotropic acid. So the method of Moeller[76] was used. According to this method, injurious effects of free acid in vegetable, mineral or synthetic tanning agents are eliminated by means of ammonium or an organic base, or by means of an ammonium salt, which retards the hydrolyzing action of the acid on the hide substance. Therefore in this experiment 30 per cent of chromotropic acid was neutralized with NH_4OH, 30 per cent of $(NH_4)_2SO_4$ added and the mixture suspended in water. The tanning was the same as in the previous experiment with chloro-H-acid, yielding a fairly soft and good leather of greenish color.

Experiment 16. Special Tanning with 1:5-Dihydroxynaphthalene.—1:5-Dihydroxynaphthalene is rather insoluble the same as is a-naphthol, and resembles the latter in producing no tannage in acid solutions. So the scheme used for a-naphthol was tried, *i. e.*, by using excess of 1:5-dihydroxynaphthalene in a slightly alkaline

[76] Moeller, W., Brit. Pat. 200,262. April 27, 1922. *Chemical Abstracts*, **18**, 481, (1924).

(NaOH) solution and the tanning carried out in the same manner as for a-naphthol. The result was a good leather comparable to that of a-naphthol.

Experiment 17. Tanning with Beta-Naphthol Derivatives as Acids and as Salts.—The following beta-naphthol derivatives were used:

G-acid—(2-naphthol-6:8-disulfonic acid)
Beta-hydroxy-naphthoic acid
Beta-hydroxy-naphthoic anilide
2-Naphthol-1-sulfonic acid
2-Naphthol-8-sulfonic acid
8-Nitro-1-diazo-2-naphthol-4-sulfonic acid

In the first test, the acids were used in the condition as received. In the second test, they were converted into sodium salts by NaOH till just alkaline, brought back to slightly acid condition by acetic acid, and subjected to experiment. In each case 15 per cent of the compound was used. The drum was run for three hours. The skins were hung to dry, washed and again dried. As these materials yielded the same results both as acids and as sodium salts, they are collectively reported as follows:

RESULT OF EXPERIMENT 17. TANNING WITH b-NAPHTHOL DERIVATIVES AS ACIDS AND SALTS.

	Tannage	Color	Special Remarks
G-Acid	No Tan	Colorless	Curl, hard and trans.
b-hydroxynaphthoic acid	No Tan	Grey-brown	Curl, hard and trans.
b-hydroxynaphthoic anilide	No Tan	Light-grey	Curl, hard and trans.
2-Naphthol-1-sulfonic acid	No Tan	Brown	Curl, hard and trans.
2-Naphthol-8-sulfonic acid	No Tan	Brown	Curl, hard and trans.
8-nitro-1-diazo-2-naphthol-4-sulfonic acid	No Tan	Yellow	Curl, hard and trans.

OBSERVATIONS

None of the b-naphthol derivatives gave tannage, yielding only curled, hard and transparent skins. G-acid, b-hydroxy-naphthoic acid and b-hydroxy-naphthoic anilide did not show any action and the skins were only surface-colored. 2-naphthol-1-sulfonic acid, 2-naphthol-8-sulfonic acid and 8-nitro-1-diazo-2-naphthol-4-sulfonic acid showed some penetration but produced no tannage.

Experiment 18. Tanning with Naphthol Dyes.—The following naphthol dyes were taken for the experiment:

Orange G.G.[77] made from aniline and b-naphtholdisulfonic acid G.

Newport chrome blue[78] made from tetramethyldiamidobenzhydrol and a-oxynaphthionic acid.

New blue R[79] made from b-naphthol and nitrosodimethylaniline chloride.

Alizarine green G[80] made from b-naphthoquinone sulfonic acid and 1-amido-2-naphthol-6-sulfonic acid.

Azo-Rubine[81] made from naphthionic acid and a-naphtholsulfonic acid NW.

Chromotrope 2R[77] made from aniline and chromotropic acid.

Congo corinth[82] made from benzidine, naphthionic acid and 1-naphthol-4-sulfonic acid.

Oxy-diamine black[83] made from H-acid, a-naphthylamine and tolidine.

Fifteen per cent of each dye was used and dissolved in water, and the drum was run for three hours as usual. The skins were hung to dry, washed, pressed and dried again.

Results of Experiment 18. Tanning with Naphthol Dyes.

	Tannage	Color	Special Remarks
Orange G G	No Tan	Orange	Penetrated, but papery
Newport chrome blue	Tan A	Dark-blue	Soft and full
New blue R	No Tan	Black-blue	Curl and hard
Alizarine green G	No Tan	Dark-green	Penetrated but hard
Azo rubine	Tan A+	Dark-red	Soft and full
Chromotrope 2R	Tan A+	Dark-red	Soft and full
Congo corinth	Tan B+	Pink-red	Slightly hard
Oxy-diamine black	Tan B	Black	Slightly hard

Observations

All of the derivatives of a-naphthol showed more or less tanning effects, while the b-naphthols gain the opposite result.

Experiment 19. Tanning with Non-Hydroxy Naphthalenesulfonic Acids.—The following naphthalene sulfonic acids and a-

[77] A Book, "Synthetic Dyestuffs and Intermediate Products," by J. C. Cain and J. F. Thorpe (1905), p. 65, Charles Griffin and Co., London.

[78] *Ibid.*, p. 91.

[79] *Ibid.*, p. 129.

[80] *Ibid.*, p. 131.

[81] *Ibid.*, p. 66.

[82] *Ibid.*, p. 70.

[83] R. N. Shreve, A Book, "Dyes Classified by Intermediates," (1922), Schultz No. A. 382, Chemical Catalog Co., New York.

naphthylamine as received were subjected to tanning experiments, using 15 per cent material and 3-hour drumming. The skins were hung to dry, washed and dried as before.

RESULTS OF EXPERIMENT 19. NAPHTHALENESULFONIC ACIDS AND NAPHTHYLAMINE.

	Tannage	Color	Special Remarks
α-Naphthylamine	No Tan	Violet	Curl, hard and trans.
1:5-naphthalene-disulfonic acid	No Tan	Colorless	Curl, hard and trans.
2:7-naphthalene-disulfonic acid	No Tan	Colorless	Curl, hard and trans.
1-naphthylamine-3:8-disulfonic acid	No Tan	Chocolate	Curl, hard and trans.
1-naphthylamine-3:6:8-trisulfonic acid	No Tan	Colorless	Curl, hard and trans.
2-naphthylamine-6-sulfonic acid	No Tan	Colorless	Curl, hard and trans.
2-naphthylamine-4:8-disulfonic acid	No Tan	Pinkish	Curl, hard and trans.

Experiment 20. Tanning with Sodium Salts of Naphthalenesulfonic Acids.—The above mentioned naphthalenesulfonic acids were converted into sodium salts and tanning tests were similarly conducted.

RESULTS OF EXPERIMENT 20. SODIUM SALTS OF NAPHTHALENESULFONIC ACIDS.

	Tannage	Color	Special Remarks
1:5-naphthalene-disulfonic acid	No Tan	Colorless	Penetrated but papery
2:7-naphthalene-disulfonic acid	No Tan	Colorless	Curl, trans. and papery
1-naphthylamine-3:8-disulfonic acid	No Tan	Chocolate	Curl, hard and trans.
1-naphthylamine-3:6:8-trisulfonic acid	No Tan	Colorless	Curl, hard and trans.
2-naphthylamine-6-sulfonic acid	No Tan	Colorless	Curl, hard and trans.
2-naphthylamine-4:8-disulfonic acid	No Tan	Pinkish	Curl, hard and trans.

OBSERVATIONS

No tannages were obtained with these non-hydroxy naphthalene derivatives. Some did not penetrate the skins, while others penetrated the skins without tanning them.

DISCUSSIONS ON THE CRITERION OF α-NAPHTHOL AND FURTHER PROOFS ON THE THEORY

From Experiment 1 to Experiment 20, the facts obtained are:

(1) All non-condensed derivatives of alpha-naphthol showed more or less tanning effects. A few compounds, namely, a-naphthol, chloro-H-acid, and chromotropic acid, which did not tan under ordinary conditions showed their tanning effects under special conditions, and since such conditions did not change the chemical composition of these compounds, the tannages produced could be said to be due to these compounds alone.

(2) All non-condensed derivatives of beta-naphthol did not produce tannage. They either had no action on the skins, did not penetrate them, or penetrated them without tanning.

(3) All the dyes derived from the naphthols penetrated the skins. Those from alpha-naphthol produced a tannage while those from beta-naphthol did not have such effects.

(4) Pure alpha-naphthylamine penetrated and strongly colored the skin, but produced no tannage.

(5) Naphthalenesulfonic acids and salts free from naphthol groups did not show any tanning action, regardless as to whether the sulfonic groups were in the alpha or beta positions.

(6) Naphthylaminesulfonic acids and salts free from naphthol groups did not show any tanning effects, nor any remarkable actions on the skins, regardless of the positions which the amino or sulfonic groups occupied.

From all these facts it is evident that alpha-naphthol is the nucleus of all a-naphthol derivatives which give tannages, and the criterion for the tanning properties of all the non-condensed naphthalene derivatives, for all naphthalene derivatives free from the naphthol group did not have any tanning effects, and among the naphthol derivatives, those from b-naphthol did not produce any tannage.

A few fragmental supports to the above generalizations are also found in the literature. In the British Patent[84] 111,141, 1-naphthol-4-sulfonic acid and 5:5-dihydroxy-2:2-dinaphthylamine-7:7-disulfonic acid were claimed as tanning agents, and in U. S. Patent[85] 1,203,069, the urea of 2-amino-5-naphthol-7-sulfonic acid was claimed. All three compounds contain a hydroxy (OH) group in an alpha position for each naphthalene nucleus. In other

[84] British Patent 111, 141, May 17, 1917, by James Yate Johnson.
[85] U. S. Patent 1,203,069, Oct. 31, 1917, by E. Stiasny & O. Schmidt.

words, they all are derivatives of alpha-naphthol. The literature[86] from 1882-1927, reveals only one non-condensed beta-naphthol derivative as claimed (Brit. Pat. 111,141) to be a tanning agent, which is 2-naphthol-6-sulfonic acid or Schaeffer's acid. But it was pointed out in the first part of this investigation that this compound has no tanning effects.

The facts mentioned also show that amino, sulfonic, chloro, nitro, diazo and carboxyl groups are not the primary tanning groups; and that only the (OH) group directly attached to the naphthalene rings at an alpha position is capable of effecting tannage. Therefore the theory is well proven that the hydroxy group or groups in a chemical compound is the primary combining agent.

Balancing Effects of Acid and Basic Groups in the Naphthalene Rings.

The experiments enumerated have developed the generalization that alpha-naphthol derivatives possess tanning properties. It was found that some alpha-naphthol derivatives tanned better than others and that there were a few which tanned only under special conditions. From observations and information furnished by the literature it would appear that the last mentioned condition is due to the hydrolytic action of the sulfonic groups present in the naphthalene rings. According to W. Moeller,[87] the syntans alone cause appreciable hydrolysis, which rapidly increases with increasing concentration. The hydrolytic action of the syntans is attributed to the action of their sulfonic acids, which split the micellar groups of the hide fibres into micels, break down the micels into protein molecules, and then hydrolyze the protein, combining with the hydrolytic products and the free amino acids to form easily soluble condensation products.

Grasser[88] demonstrated the hydrolytic and solubilizing actions of the sulfonic acid groups on the hide substance by allowing the following naphthalenesulfonic acids to act on pelt for 12 days:

(1) Concentrated solution of a-naphthalenesulfonic acid (10° Bé).

[86] *Journal of the Society of Chemical Industry*, 1882-1906, *Chemical Abstracts*, 1907-1927.

[87] "The Behavior of Synthetic Tannins, Containing Sulfonic Groups," W. Moeller, *Collegium* (1920), 520-36.

[88] Grasser, G., A. Book, "Synthetic Tannins," The English translation by Enna (1922), p. 95, Van Nostrand Co., New York.

(2) Concentrated solution of b-naphthalenesulfonic acid (6° Bé).

(3) Concentrated solution of 2,7-naphthalenedisulfonic acid (18° Bé).

and he found that solution (1) swells the pelt to a considerable extent without, however, solubilizing it. Solution (2) produces a similar effect. Solution (3) dissolves the pelt appreciably on the first day and the solubilization is complete after 6 days. Grasser explains the different behavior of the mono- and disulfonic acids in their differences in solubilities, and acidities.

The hydrolytic action of the typical synthetic tannin, "Neradol D" was also studied by Grasser[89] who allowed solutions of Neradol D at different concentrations to act on pelts for 10 days, and then washed them in running water for 24 hours. When the pelts thus treated had become dry, those treated by 33° Bé[90] and by 30° Bé solutions were completely gelatinized, and those by solutions below 5° Bé appeared normally tanned.

Grasser[88] explains the hydrolytic and solubilizing actions of the synthetic tannins as due to the acidity.

Moeller[91] also has the same opinion. According to his idea, synthetic tannins do not behave like other tanning agents but like mineral acids, which hydrolyze the hide substance in proportion to the time and concentration. Free H-ions dissociated from the free acids have a gradual destructive effect on hide substance even when it is converted into leather.

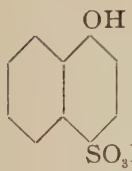
Although the free acids or the free H-ions present in the synthetic tannins are powerful hydrolyzing and solubilizing agents, the hydrolyzing and solubilizing effects of the synthetic tannins should be attributed to the sulfonic groups as a whole and not to the free H-ions alone, for under the conditions of these experiments, it was found that certain naphtholsulfonic acids still exerted the hydrolyzing and solubilizing actions on the skins even after they had been converted into sodium salts. This conception is in accord with the fact found in the experiments that the more the sulfonic groups in the naphthalene rings, whether in form of

[89] *Ibid*, p. 117.
[90] *Collegium* (1913), 521, 487.
[91] Moeller, W., "Nägeli Micellar Theory," *Z. Leder-u. Gerb.-Chem.* **2**, 45-90 (1922).

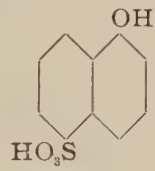
acid or salt, the higher is the gelatinizing action and the less the tanning effect. This is the reason why chromotropic acid, being an a-naphthol derivative, did not exert any tannage, and produced highly gelatinized skin under ordinary conditions of tanning.

This new conception of the sulfonic groups explains the abnormal phenomena existing in the tanning with naphtholsulfonic acids, and may be utilized to predict the relative tanning effects of these compounds. It was noticed that as the sulfonic groups increased, the less efficient the compound became as a tanning agent. When there is one sulfonic group and one amino group in the a-naphthol compound, a balancing condition is established, and good tannage results. If there are two sulfonic groups and one amino group in the a-naphthol compound, the tanning effects are less. When there is no amino group in the rings and more than one sulfonic group present, the compound usually yields a gelatinized skin. It may be reasonably concluded from this that when the acid groups in an alpha compound are balanced by basic groups, such as the amino group, a better tannage is obtained than when they are not balanced. The following are examples which will serve to demonstrate this principle:

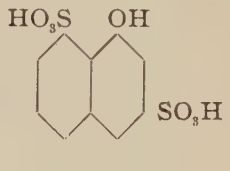
(1) Comparison of 1-naphthol-4-sulfonic acid and 1-naphthol-5-sulfonic acid with 1-naphthol-3:8-disulfonic acid:



Mono-sulfonic acid.



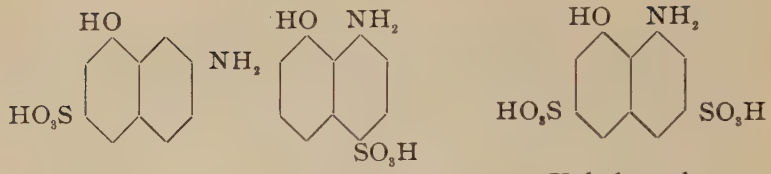
Mono-sulfonic acid.



Disulfonic acid.

The two mono-sulfonic acids exerted but very little gelatinizing action and procured a good tannage, while the disulfonic acid gelatinized the skin and yielded a poor tannage.

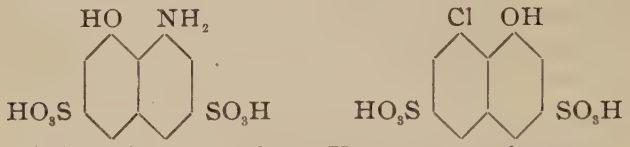
(2) Comparison of 2-amino-8-naphthol-6-sulfonic acid and 1-amino-8-naphthol-4-sulfonic acid, with 1-amino-8-naphthol-3:6-disulfonic acid:



Balanced. Balanced. Unbalanced.

The balanced compounds tanned very well, while the unbalanced one produced a very inferior leather.

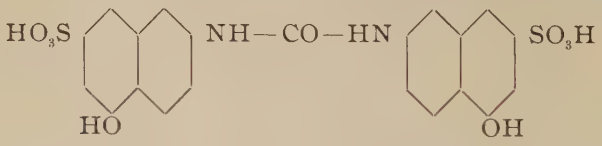
(3) Comparison of 1-amino-8-naphthol-3:6-disulfonic acid with 1-naphthol-8-chloro-3:6-disulfonic acid.



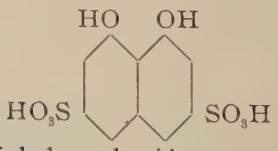
Unbalanced compound. Uncompensated compound.

The unbalanced compound tanned much better than the uncompensated compound. In fact the substitution of the basic NH_2 group by the acidic Cl group nearly deprives it of all the tanning properties of the amino compound.

(4) Comparison of 5:5-dihydroxy-7:7-disulfonic-2:2-dinaphthyl urea[92] and 1:8-dihydroxynaphthalene-3:6-disulfonic acid:



Balanced acid and basic groups.



Unbalanced acid groups.

In the first compound, the acid and basic groups are most balanced and therefore as would be expected it gave an excellent

[92] Formula found in the book "The Manufacture of Intermediates for Dyes," by J. C. Cain (1919), p. 240, MacMillan & Co., London.

tannage. In the second compound all 4 groups are acidic in reaction, and therefore it produced a highly gelatinized skin, which showed no tanning effects.

(5) Comparison of chromotropic acid and chromotrope 2R, the red Dye.

Although chromotropic acid, having 4 acid groups in the rings and no basic groups to compensate them, showed no tannage under ordinary conditions, its derivatives, chromotrope 2R, gave rather good tannage under the same conditions, because chromotrope 2R contains a basic element, aniline, as the balancing factor.

(6) Further proofs of the balancing principle are shown by the fact that all alpha-naphthol derivatives tanned much better than chromotropic acid and chloro-H-acid, because in the latter two compounds there are 4 acidic groups in the rings with no basic groups to balance them.

Conversion of Inactive into Active Tanning Materials.—In the gelatine tests, it was noticed that the addition of ferric chloride to the mixtures of naphtholsulfonic acids and 3 per cent gelatine solution caused a change in color in some cases, and a heavy precipitation in others. Ferric chloride alone or the naphtholsulfonic acids alone, however, did not give a precipitate with the gelatine. Neither did the mixtures of ferric chloride and the naphtholsulfonic acids form any precipitate. When, however, these mixtures were added to the gelatine solution heavy precipitates were usually obtained. Since the precipitation occurred even in acid solution, it could not be ferric hydroxide, but must be of a complex structure. This phenomena led to the idea that mixtures of ferric chloride and naphtholsulfonic acids might constitute a good tanning complex, by virtue of their ability to precipitate gelatine. Accordingly, experiments were conducted to determine the tanning properties of these mixtures.

Experiment 21. Tanning with Naphtholsulfonic Acids in Presence of Ferric Chloride.—The following naphtholsulfonic acids were used in this experiment.

H-acid—(1-amino-8-naphthol-3:6-disulfonic acid)
Oxy-Laurent's acid—(1-naphthol-5-sulfonic acid)
Schaeffer's acid—(2-naphthol-6-sulfonic acid)
Gamma acid—(2-amino-8-naphthol-6-sulfonic acid)
Nevile and Winther's acid—(1-naphthol-4-sulfonic acid)
e-acid—(1-naphthol-3:8-disulfonic acid)
F-acid—(2-naphthol-7-sulfonic acid)
R-acid—(2-naphthol-3:6-disulfonic acid)

Fifteen per cent naphtholsulfonic acid was used in each case. Since concentrated ferric chloride solution will produce a tannage the amount of the reagent used must be very small. Therefore, only 0.2 cc. of 10 per cent ferric chloride solution was employed for each gram of skin, in other words 25 grams of skin would take 5 cc. of a 10 per cent ferric chloride, or 0.5 gram of pure ferric chloride. A blank test was made with ferric chloride in the same proportion as used for its mixtures, but no tannage resulted. The drum was run for 3 hours. The skins were hung to dry, washed, and dried again.

RESULTS OF EXPERIMENT 21. NAPHTHOLSULFONIC ACIDS IN PRESENCE OF FERRIC CHLORIDE.

	Tannage	Color	Special Remarks
H-Acid	Tan A	Dark-brown	Soft and full
Oxy-Laurent's Acid	Tan A	Green-blue	Soft and full
Schaeffer's Acid	Tan B	Light-grey	Slightly hard
Gamma Acid	Tan A	Dark-brown	Soft and full
Nevile & Winther's Acid	Tan A+	Light-pink	Very soft and full
e-Acid	Tan A+	Light-brown	Very soft and full
F-Acid	Tan A	Grey-black	Soft and full
R-Acid	Tan B	Light-pink	Slightly papery
Blank (Pure $FeCl_3$)	No Tan	Yellow	Hard and Trans.

OBSERVATIONS

The most remarkable observation was that in the presence of a small amount of ferric chloride, both a- and b-naphtholsulfonic acids showed more or less tannage. The e-acid being an unbalanced compound produced somewhat gelatinized skin when used alone, but gave excellent tannage when used in presence of ferric chloride. Another feature of this kind of tannage was that the washed skins had a "tanned feel" when still wet, *i. e.*, they did not feel slippery or gelatinous when soaked in water. It should be noted that the "blank skins" were not tanned under such conditions.

Experiment 22. Tanning with Naphtholsulfonic Acids and Other Metallic Salts.—Since ferric chloride had been observed to have improved remarkably the tanning properties of the naphtholsulfonic acids, other metallic salts were similarly tried in order to investigate the nature of such complex tanning reactions. Ten per cent solutions of $Cr_2(SO_4)_3$, $Al_2(SO_4)_3$, $CuSO_4$, $MnCl_2$ were used. Fifteen per cent naphtholsulfonic acid was used in each

case. Again only 0.2 cc. of 10 per cent solution of each metallic salt was used for each gram of skin. The drumming was run for 3 hours, and the skins were hung to dry, washed and dried again, as usual.

RESULTS OF EXPERIMENT 22. NAPHTHOLSULFONIC ACIDS AND OTHER METALLIC SALTS.

	$Cr_2(SO_4)_3$	$Al_2(SO_4)_3$	$CuSO_4$	$MnCl_2$
H-Acid	Tan A	Tan B	Tan B	Tan B
Oxy-Laurent's Acid	Tan A	Tan B	Tan B	Tan B
Schaeffer's Acid	Tan B	Some Tan	No Tan	No Tan
Gamma Acid	Tan A+	Tan A	Tan A	Tan A
Nevile & Winther's Acid	Tan A+	Tan A	Tan A	Tan A
e-Acid	Tan A	Tan B	Tan B	Tan B
F-Acid	Tan B	Some Tan	No Tan	No Tan
R-Acid	Tan B	Some Tan	No Tan	No Tan
Blank (Pure metallic salt)	Tan B	Some Tan	No Tan	No Tan

OBSERVATIONS

In general, these salts behaved much differently from ferric chloride. They did not improve the tanning power of alpha-naphthol sulfonic acids, nor induce any tanning properties to the b-naphtholsulfonic acids. The salts, such as $Cr_2(SO_4)_3$, which possess tanning properties themselves, may be used to advantage to impart a share of their tanning effects to the skins, when mixed with the naphtholsulfonic acids, while those non-tanning salts such as $CuSO_4$ and $MnCl_2$ are useless for this purpose.

Experiment 23. Tanning with a- and b-naphthols in Presence of $FeCl_3$.—Since ferric chloride improved the tanning properties of a-naphtholsulfonic acids and converted the inactive b-naphtholsulfonic acids into active tanning materials, its action was investigated in conjunction with the pure naphthols. From the previous investigation, it was learned that tanning experiments with the pure naphthols could be conducted either in alkaline or in alcoholic solutions. But in connection with ferric chloride, alkaline solutions would throw out all the iron as precipitate, so only alcoholic solutions were available for such experiments.

In accordance with previous experiments on the pure naphthols, 50 per cent of the naphthol was dissolved in 100 cc. denatured alcohol, and added with a calculated amount of ferric chloride solution, *i. e.*, 0.2 cc. 10 per cent ferric chloride solution per gram of skin. The drumming was carried for 3 hours. The skins were hung up to dry, washed, and dried again as usual.

RESULTS OF EXPERIMENT 23. TANNING WITH NAPHTHOLS IN PRESENCE OF FERRIC CHLORIDE.

	a-Naphthol + $FeCl_3$	b-Naphthol + $FeCl_3$
Tannage	Tan A	Tan A
Curling	No Curl	No Curl
Feeling	Soft	Soft
Transparency	Opaque	Opaque
Greasiness	Non-greasy	Non-greasy
Penetration	Thorough	Thorough
Coloration	Pink	Colorless

OBSERVATIONS

Both a- and b-naphthol yielded tannage in the presence of ferric chloride. It is to be remembered that b-naphthol alone or $FeCl_3$ alone did not tan, but it is interesting that their mixture did tan.

Experiment 24. Tanning with Other a-Naphtholsulfonic Acids in Presence of Ferric Chloride.—Fifteen per cent a-naphtholsulfonic acid was used as the main tanning material and 0.2 cc. 10 per cent ferric chloride solution per gram of skin was taken as the accelerating agent. The drumming was carried on for 3 hours. The skins were hung to dry, washed, and dried again, as before.

RESULTS OF EXPERIMENT 24. OTHER a-NAPHTHOLSULFONIC ACIDS IN PRESENCE OF FERRIC CHLORIDE.

	Tannage	Color	Special Remarks
S-Acid	Tan A	Black	Soft and thoroughly penetrated
J-Acid	Tan A	Grey	Soft and thoroughly penetrated
Chicago acid	Tan A+	Green	Very soft and full
Phenyl Gamma acid	Tan A	Green-grey	Soft and thoroughly penetrated
Phenyl-J-acid	Tan A+	Green-grey	Very soft and full
Chloro-H-acid	Tan A+	Light-brown	Very soft and full
Chromotropic acid	Tan B—	Light-green	But slightly hard
1:5-Dihydroxynaphthalene	No Tan	Light-grey	Curl, hard but opaque
I-acid Imid	Tan A+	Green-brown	Very soft and full
Rhoduline acid	Tan A+	Green-brown	Very soft and full
J-acid Urea	Tan A+	Light-brown	Very soft and full
Blank (pure $FeCl_3$)	No Tan	Light-yellow	Curl, hard, trans.

OBSERVATIONS

All the a-naphtholsulfonic acids tanned better in presence of $FeCl_3$ than they did alone. Chloro-H-acid did not tan under ordinary conditions but tanned well in presence of $FeCl_3$. Chromotropic acid also tanned in presence of $FeCl_3$, but not so well as

others. 1:5-Dihydroxynaphthalene did not tan in presence of $FeCl_3$, because it was too insoluble in water; its alkaline solution gave better tannage, but could not be used in connection with ferric chloride.

Experiment 25. Tanning with Other b-Naphthol Derivatives, in Presence of Ferric Chloride.—Fifteen per cent b-naphtholsulfonic acid was used in each case as the main tanning material and 0.2 cc. 10 per cent ferric chloride per gram of skin was used as the converting agent. The drumming was carried on for 3 hours. The skins were hung to dry, washed, and dried again, as before.

RESULTS OF EXPERIMENT 25. OTHER b-NAPHTHOL DERIVATIVES IN PRESENCE OF FERRIC CHLORIDE.

	Tannage	Color	Special Remarks
G-acid	Tan B	White	Opaque, slightly hard
b-hydroxynaphthoic acid	Tan A	Green-grey	Opaque, soft and full
b-hydroxynaphthoic anilide	Tan B	Light-grey	Opaque, slightly hard
2-naphthol-1-sulfonic acid	Tan A+	Light-brown	Very soft and full
2-naphthol-8-sulfonic acid	Tan A+	Light-violet	Very soft and full
8-nitro-1-diazo-2-naphthol-4-sulfonic acid	Tan A	Yellowish	Opaque, soft and full

OBSERVATIONS

It is interesting to note that the b-naphthol derivatives did not tan either as acids or as salts, but tanned in the presence of ferric chloride. Those which did not tan so well as others were due to their low solubilities. The active tanning agent was not ferric chloride as shown by the fact that the same amount of ferric chloride alone used in the blank test did not yield leather.

DISCUSSION ON THE REACTIONS OF FERRIC CHLORIDE AND NAPHTHOL DERIVATIVES

The above experiments definitely show that ferric chloride is the accelerating agent for tanning with a-naphthol derivatives, and a converting agent for b-naphthol derivatives changing inactive into active tanning materials. These conceptions are also suggested by the gelatine tests. In the first place, when ferric chloride was added to naphthol derivatives, characteristic color reactions oc-

curred, and the change in color indicated a chemical change. In the second place, the reaction products from ferric chloride and the naphthol derivatives were found to precipitate gelatine. The precipitation of gelatine is a general indication of tanning properties, as most of the synthetic as well as vegetable tannins show this characteristic reaction.

However, these facts can be more clearly explained by the reaction of ferric chloride with pure naphthols. According to Richter,[93] from the aqueous solution of alpha-naphthol, ferric chloride precipitates violet flakes of a-dinaphthol, and in beta-naphthol solution, ferric chloride imparts a greenish color and separates b-dinaphthol. Perkin and Kipping[94] think that this is an oxidation, condensation or complex reaction, forming probably an iron compound of the dinaphthol, $HO.C_{10}H_6C_{10}H_6.OH$. Based on Perkin and Kipping's idea, the reactions between ferric chloride and the naphthols may be worked out as follows:

The first reaction may be a condensation process, resulting in the formation of a di-naphthol:

$$2C_{10}H_7.OH + 2FeCl_3 =$$

Naphthol $\qquad HO.C_{10}H_6.C_{10}H_6.OH + 2FeCl_2 + 2HCl$

Dinaphthol

The second reaction may take place between the dinaphthol and ferric chloride, forming a complex iron compound:

$$FeCl_3 + 3HO.C_{10}H_6.C_{10}H_6.OH =$$

$$Fe(O.C_{10}H_6.C_{10}H_6.OH)_3 + 3HCl$$

The second reaction is quite possible, as shown by the fact that only a small amount of ferric chloride was required to convert the inactive b-naphthol derivatives into active tanning materials. In the resulting product from the second reaction, only 1 mole of iron is required to combine with 6 moles of the naphthol. Since the $FeCl_3$ reaction is general for both a- and b-naphthol, it explains the reason why b-naphthol derivatives also tanned in presence of ferric chloride.

[93] "Richter's Organic Chemistry," Translated by E. E. F. D'albe (1922), p. 665, Blakiston's Son & Co., Philadelphia.

[94] "Organic Chemistry" by W. H. Perkin & E. S. Kipping (1923), p. 508, J. B. Lippincott Co., Philadelphia.

In the tanning process, the second reaction may be reversible, in that ferric chloride is regenerated, and tans the skin in accordance with the general tanning reactions of ferric chloride, or it may combine with the skin according to the chemical theory of tannage by Wilson. In the opinion of the writer the dinaphthol set free effects the main tanning reactions by combining with the amino groups of the hide substance to form leather, according to the proposed theory of "active hydroxyl groups":

$$\begin{matrix} R{-}N\begin{matrix} H \\ H \end{matrix} \\ \text{(Hide)} \end{matrix} + \begin{matrix} HO.C_{10}H_6.C_{10}H_6.OH \\ HO.C_{10}H_6.C_{10}H_6.OH \\ \text{(Dinaphthol)} \end{matrix} =$$

$$R{-}N\begin{matrix} C_{10}H_6.C_{10}H_6.OH \\ C_{10}H_6.C_{10}H_6.OH \\ \text{(Leather)} \end{matrix} + 2\ H_2O$$

This is the most favorable reaction for leather formation when 1 amino, NH_2, group combines with 4 residues of naphthalene. Poor tannage occurs when 1 amino, NH_2, group combines with a less number of naphthalene residues.

Analogy between the formaldehyde and ferric chloride condensations.—It is interesting to find that the condensation induced by ferric chloride is very similar to that induced by formaldehyde. Such analogy can be shown in the following points:

(1) Formaldehyde induces the condensation of phenols in forming a product containing 2 residues of phenol, while ferric chloride induces the condensation of naphthols, in forming a product containing 2 residues of naphthol.

$HO.C_6H_4.CH_2.C_6H_4.OH$	$HO.C_{10}H_6.C_{10}H_6.OH$
Formaldehyde-Phenol	$FeCl_3$-Naphthol
Condensation Product	Condensation Product

(2) Formaldehyde-phenol condensation products are insoluble, especially in alkaline solution, and $FeCl_3$-naphthol condensation products are also insoluble in aqueous solution.

(3) Condensation products of phenolsulfonic acids and formaldehyde are water-soluble, and condensation products of naphtholsulfonic acids and ferric chloride are also soluble in water.

(4) Condensation products of phenolsulfonic acids and formaldehyde precipitate gelatine, and similarly condensation products of naphthsulfonic acids and ferric chloride precipitate gelatine.

(5) Condensation products of phenolsulfonic acids and formaldehyde possess tanning properties, giving rise to the synthetic tannins called neradols, while condensation products of naphtholsulfonic acids and ferric chloride also show remarkable tanning effects.

All those points indicate that the condensation induced by formaldehyde is very similar to that by ferric chloride, the only difference being that the condensation product of ferric chloride does not contain the CH_2 group.

However, we have two classes of condensation products going hand in hand, and since the condensation products of formaldehyde and phenol-sulfonic acids or naphtholsulfonic acids all show tanning properties, there is no reason why the condensation products of ferric chloride and naphtholsulfonic acids should not show the same, if not better, tanning properties, because condensation products of naphtholsulfonic acids have much larger molecules.

Behavior of Other Organic Compounds as Tanning Agents.—In order to investigate further the "hydroxy theory" miscellaneous organic compounds were subjected to tanning experiments.

Experiment 26. Tanning with Phenol and Its Homologues.—Since phenol and its homologues also contain the hydroxy group or groups, these were naturally tried first. The various phenolic compounds were first made soluble by NaOH till just alkaline, and then acidified with acetic acid. About 15 per cent materials were used. But in case of cresol, 20 cc. of the mixed product were dissolved in 50 cc. of denatured alcohol, and in case of thymol, 30 per cent of the crystalline material was dissolved in 50 cc. of denatured alcohol. The other materials were all in water solutions. The drumming was carried on for 3 hours. The skins were hung to dry, washed and dried, as usual.

RESULTS OF EXPERIMENT 26. TANNING WITH PHENOL AND ITS HOMOLOGUES.

	Tannage	Color	Special Remarks
Phenol	No Tan	Colorless	Curl, hard, trans.
Catechol	No Tan	Colorless	Curl, hard, trans.
Resorcinol	No Tan	Colorless	Curl, hard, trans.
Gallic acid	No Tan	Dark-brown	Curl, hard, trans.
Salicylic acid	No Tan	Colorless	Curl, hard, trans.
Cresols	No Tan	Light-grey	Curl, hard, trans.
Thymol	No Tan	Colorless	Curl, hard, trans.

OBSERVATIONS

None of these simple phenol derivatives showed any tanning effects. Even catechol and gallic acid, which are derived from the natural tannins, did not give any tannage as simple compounds. These results strengthen the idea of Bamberger[95] that at least three residues of phenol derivatives are necessary for tanning properties.

Experiment 27. Tanning with Non-Hydroxy Benzene Derivatives.—Since most of organic liquids were very penetrating and irritating to the skins, they were expected to have some action, if not tanning effects on the pelt. Therefore, some common organic liquids were taken for experiment. Fifty cc. of each liquid were used for about 25 grams of skin. The usual drumming process was followed.

RESULTS OF EXPERIMENT 28. TANNING WITH ORGANIC LIQUIDS.

	Tannage	Color	Special Remarks
Benzaldehyde	No Tan	Light-brown	Curl, hard, trans.
Nitrobenzene	No Tan	Light-yellow	Curl, hard, trans.
Benzyl chloride	No Tan	Light-brown	Curl, hard, trans.
Benzoyl chloride	No Tan	Light-pink	Curl, transparent,

OBSERVATIONS

Although these organic liquids thoroughly penetrated the fibres of the skin, but they did not stay with the fibres, and quickly evaporated off upon drying. Benzoyl chloride attacked the skins rather severely, which, when dried, became very weak and could be pulled apart easily. However, benzoyl chloride did not give any tannage.

[95] Bamberger, H., Basel. *Chem. Ztg.* **43**, 318 (1919).

Experiment 29. Tanning with Miscellaneous Dyes.—The following miscellaneous dyes were used in the experiment:

Chrome green[78]	Made from tetramethyldiamidobenzhydrol + benzoic acid.
Diamond flavine[81]	Made from tetrazobenzidine + salicylic acid.
Azo dark green[96]	A triphenylcarbinol dye, containing 2 moles of dimethylaniline and 1 mole of azo-salicylic acid.
Bismarck brown[97]	Made from 3 moles of m-phenylene-diamine.
Cyanole extra[98]	A triphenylcarbinol dye, containing 2 moles of methyl-ethylaniline and 1 mole of phenoldisulfonic acid.
Pure soluble blue[99]	A triphenylcarbinol dye, prepared by heating aniline or toluidine with rosaniline followed by sulfonation.
Violamine 2R[100]	Made from phthalic anhydride + 2 moles of resorcin + 2 moles of toluidine followed by sulfonation.
Indazine M[101]	Made from nitrosodimethylaniline + diphenyl-m-phenylenediamine.
Primuline yellow[102]	Prepared by heating p-toluidine with sulphur.
Resorcin brown[103]	Made from resorcinol + m-xylidine + sulfanilic acid.
Diamineral brown G[104]	Made from 2 moles of ethyl-2-naphthylamine-7-sulfonic acid + tolidine
Thioflavine S[105]	Prepared by methylation of primuline.

About 15 per cent material was used in each case, dissolving or suspending in about 50 cc. water. The drumming was carried for 3 hours, and then the skins were taken out and hung to dry overnight. They were thoroughly washed in plain water, and dried in air.

[96] A Book, "Synthetic Dyestuffs and Intermediate Products" by J. C. Cain & J. F. Thorpe. (1905), p. 55. Charles Griffin & Co., London.

[97] *Ibid.* p. 72.

[98] *Ibid.* p. 81.

[99] *Ibid.* p. 92, 328.

[100] *Ibid.* p. 102.

[101] *Ibid.* p. 141.

[102] *Ibid.* p. 153.

[103] A Book, "Dyes Classified by Intermediates" by R. N. Shreve, (1922), Schultz No. 211. Chemical Catalog Co., New York.

[104] *Ibid.* Schultz No. A372.

[105] *Ibid.* Schultz No. 615.

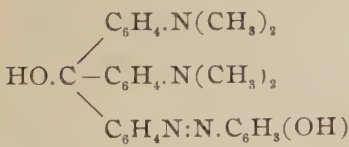
RESULTS OF EXPERIMENT 29. TANNING WITH MISCELLANEOUS DYES.

	Tannage	Color	Special Remarks
Chrome green	Some Tan	Dark-green	Opaque, cracky surface
Diamond flavine	Tan B	Yellow-brown	Opaque, semi-soft
Azo Dark green	Tan B	Dark-green	Opaque, semi-soft
Bismarck Brown	No Tan	Dark-brown	Opaque, curl, hard
Cyanole extra	Tan A+	Violet-blue	Very soft and full
Pure soluble blue	Tan A+	Blue-violet	Very soft and full
Violamine 2R	Tan A+	Deep-violet	Very soft and full
Indazine M	No Tan	Dark-violet	Opaque, curl, hard
Primuline yellow	Tan A+	Yellow	Very soft and full
Resorcin Brown	Tan A	Brown	Opaque, soft, full
Diamineral Brown G	No Tan	Dark-brown	Opaque, curl, hard
Thioflavine S	Tan A+	Yellow	Very soft and full

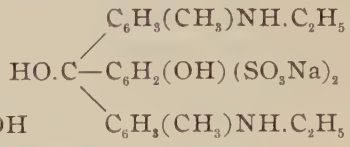
OBSERVATIONS

Most of the dyes more or less tanned, due to their complex structures and large molecules. Since these dyes consist of aggregates of different groups, the determination of their tanning groups is rather difficult. However, those dyes which have the structure of "triphenyl carbinol" are particularly notable for their tanning effects, and for their connection with the "hydroxy theory," and therefore will be discussed in a separate section.

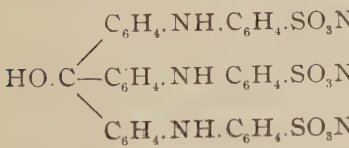
Significance of the (OH) Group in Triphenylcarbinol Structure.—In the tanning with the dyes, it was noticed that dyes having the triphenylcarbinol structure showed more or less tanning effects. In this investigation, four dyes of this structure were found to have tanning properties, namely,



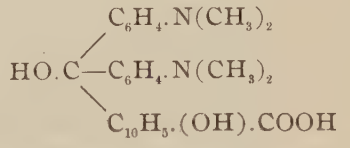
(Base of Azo Dark Green[96])



(Base of Cyanole Extra[98])



(Base of Pure Soluble Blue[99])

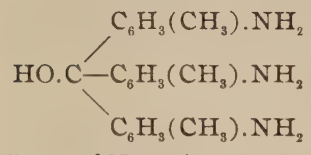


(Base of Chrome Blue[78])

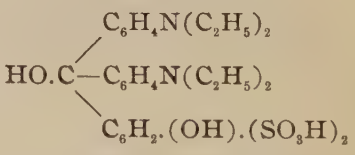
It is easily seen that all these dyes have an (OH) group attached to the central carbon, forming the carbinol group.

In the chemistry of making these dyes, it is a well known fact that the general process is first to prepare the "leuco base," H.C. (phenyl residue)$_3$, and then oxidize the remaining H to (OH) group to form the "color base," HO.C. (phenyl residue)$_3$, and finally dissolve the color base in acid to form the dye. At any rate, the color base is the nucleus for forming all the triphenylmethane dyes, although the color is varied by other groups, such as NH_2, $N(CH_3)_2$, etc. Quoting from Cain and Thorpe,[106] the following sentence is interesting: "Probably no other series of dyestuffs illustrate to such a marked extent the influence of the auxochrome groups, NH_2 and OH, as the compounds of the triphenylmethane series."

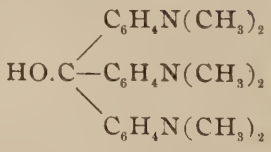
Here it was found that this "color base," essentially the (OH) group attached to the triphenyl carbon, is not only capable of forming many dyes but also capable of converting pelt into leather. Besides the above four dyes found in this investigation to have exhibited their tanning properties, other dyes of similar structure may also be cited. Zacharias[107] converted pelt into leather by the action of many coal tar dyes, while Herzog and Alder[108] obtained leather by using Newfuchsine, Patent Blue V, and Crystal Violet. The latter three dyes have the following structures.



(Base of New Fuchsine)



(Base of Patent Blue V)



(Base of Crystal Violet)

Although in presence of acids, these formulae are usually represented in the literature with the disappearance of the (OH) group

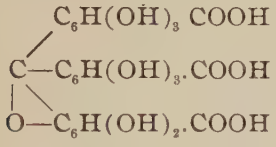
[106] A Book, "Synthetic Dyestuffs and Intermediate Products," by J. C. Cain & J. F. Thorpe (1905), p. 95. Charles Griffin & Co., London.

[107] *Zeits. F. Ang. Chem.*, **21**, 1645 (1907).

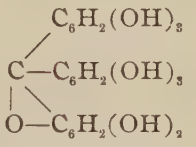
[108] Grasser's Book, "Synthetic Tannins," The English Translation, (1922) by Enna, p. 75, Van Nostrand Co., New York.

in order to fulfill the "chromophore" theory, these color bases, HO.C. (phenyl residue)$_3$ will still exist in presence of water.

The development of the color base of the triphenylcarbinol dyes, as the effective tanning group of this series, is quite reasonable, when we look back to the "Tannophor Theory" of Nierenstein. Basing on VonBaeyer's observation, Nierenstein found that when formaldehyde was added to gallic acid, in addition to the insoluble hexahydroxydiphenylmethanedicarboxylic acid, a soluble product was formed which precipitated gelatine. Nierenstein identified this latter product to be hexahydroxyaurinecarboxylic acid. The reaction of formaldehyde and pyrogallol also yielded similar products. These soluble products are represented as follows:



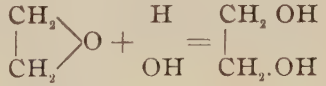
(From Gallic Acid)

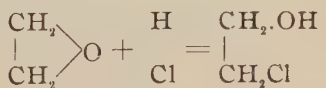


(From Pyrogallol)

Nierenstein was keen in observing that there existed an effective tanning group in the triphenyl carbon, and he considered that the effective tanning group was —CO—, or a "tannophor" group, which gave rise to the tanning properties of all these compounds.

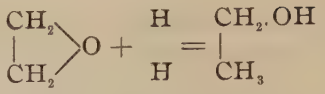
However, when we look over the structures of these compounds again, we will notice that such structures are but those of "inner ethers," and in general, inner ethers are very unstable and ready to unite with nearly all chemical reagents,[109] such as water, halogen acids, nascent hydrogen, etc. These reactions can be examplified by means of ethylene oxide, a typical inner ether.

(1) Reaction with water 

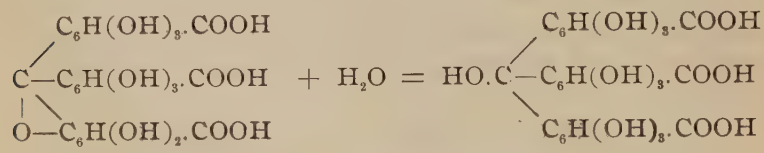
(2) Reaction with HCl 

[109] A Book, "Theoretical Organic Chemistry," by J. B. Cohen (1920), p. 275-6. MacMillan & Co., London.

(3) Reaction with H_2

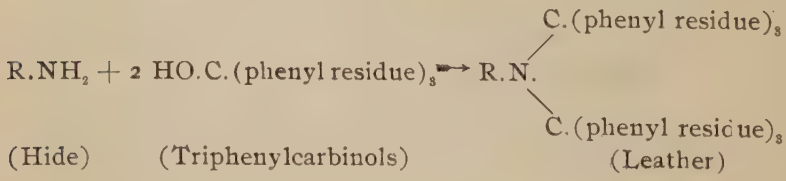


Now in tan liquors the first reaction, *i. e.*, with water, is most important, and naturally the inner ethers of Nierenstein will inevitably be converted into the corresponding hydroxy compounds, similar to the color bases of the triphenylmethane dyes, as follows:



In fact, the inner ethers of Nierenstein should never exist as far as there is water present, nor such inner ethers can be made in an excess of water. Therefore, the hypothesis of Nierenstein as to the existence of a tannophor group —CO— is entirely unsound, and should be changed to that of "hydroxy group" which has also been proven to exist as color base of the triphenylmethane dyes.

Now it has been systematically proven that the hydroxy group, OH, is taking the place of the tannophor group, —CO—, of Nierenstein, and it can be further shown that this hydroxy (OH) group attached to the triphenylcarbinol is the real tanning group, by the fact that such dyes as pure soluble blue, new fuchsine, and crystal violet, contain no other hydroxy group except that attached to the triphenylcarbinol carbon, and therefore their tanning properties must be due to this particular hydroxy group. In the present theory of leather formation, the combination of these compounds can be represented as follows:



Here it is easily seen that every one of the amino, NH_2, group in the hide substance is capable of combining with 6 or more residues of benzene, and this explains the reason why compounds of triphenylcarbinol structure are very tanning-reactive.

Hide Powder and Leather Analyses.—These analyses are insignificant for cases of synthetic tannins, where the results cannot comply with the actual tanning conditions in the plant. Moeller[110] in discussing the bating and tanning actions of the synthetic tannins pointed out that the present methods of analysis are useless for synthetic tannins. A method is needed for the separation of the combined and free sulfo-acids, and it will probably be necessary to use ultrafiltration or dialysis. According to Grasser[111] the following may be quoted: "Whereas the evaluation of vegetable tanning matters necessitates determinations of their practical applicability in addition to qualitative and quantitative analyses, the latter two determinations are of practically no value when dealing with synthetic tannins." Thus we see that hide powder analysis in the case of synthetic tannins would not express the results obtained from the actual tanning process. However, for the sake of experience, hide powder analyses were conducted with a few of the synthetic tanning materials.

Hide Powder Analysis

The commercial hide powder was used. About 2 grams of hide powder and about 1 gram of the synthetic material was used in each analysis, the exact weights being obtained for later calculations. The synthetic tanning material was dissolved in 50 cc. of distilled water contained in a large glass test tube, and the weighed hide powder added, and the mixture was thoroughly shaken, and then allowed to stand for 24 hours. The mixture was filtered through a good suction filter, and the residue thoroughly washed. The filtrate was evaporated to dryness, and then dried at 100° C. at which temperature the synthetic tanning material used had been dried before taken for analysis. Two samples were taken for each tanning material, and the results reported were averaged values from these samples.

[110] Moeller, W., *Collegium* (1921), 232-6; *Ledertechn. Rundschau.*, **20**, 154; **21**, 161, (1920).

[111] Grasser, G., A Book, "Synthetic Tannins," The English Translation by Enna, (1922), p. 77. Von Nostrand Co., New York.

RESULTS OF HIDE POWDER ANALYSIS.

	Averaged Per Cent Absorption Based on weight of Hide
1-Naphthol-4-sulfonic acid	5.83%
1-Naphthol-5-sulfonic acid	1.92%
Sodium salt of 2-amino-8-naphthol-6-sulfonic acid	2.67%
Sodium salt of 1-amino-8-naphthol-3:6-disulfonic acid	(Increase in weight)

It is remarkable to note that the disulfonic acid caused an increase in weight of the residue, although this material was observed to have thoroughly combined with the hide powder. In other words, this substance combined with the hide powder on the one hand, and dissolved some of the hide substance on the other. This phenomenon was also observed in the tanning experiments. The solubilizing effects of the naphthalenesulfonic acids have been thoroughly discussed by Grasser (see above), and in this connection the hide powder analysis is useless.

LEATHER ANALYSIS FOR IRON CONTENT

In the above investigation, ferric chloride had been found to be an accelerating agent for a-naphthol derivatives, and converting agent for b-naphthol derivatives, used for tanning materials. It was of interest to find out whether this process was an iron tannage or not. Therefore leathers produced involving the use of ferric chloride were subjected to analysis for their iron content.

In the analysis, a piece of leather, weighing about 3 to 4 grams, was accurately weighed, and then burned to drive off all organic matter, and ignited for 2 hours to convert all the iron into ferric oxide. The cooled iron residue was dissolved in concentrated HCl, filtered through filter paper and the filtrate precipitated with NH_4OH. The precipitate was dried and ignited, and the residue was weighed as Fe_2O_3. An independent determination was conducted by means of the usual permanganate method. The average results were reported as follows:

TABLE IV.—RESULTS OF LEATHER ANALYSIS FOR IRON CONTENT.

Materials Used to Produce the Leather	Averaged Per Cent Fe_2O_3 Based on Weight of Leather
1-Naphthol-5-sulfonic acid + $FeCl_3$	0.58% Fe_2O_3
1-Naphthol-4-sulfonic acid + $FeCl_3$	0.77% Fe_2O_3
b-Hydroxynaphthoic acid + $FeCl_3$	0.91% Fe_2O_3
2-Naphthol-1-sulfonic acid + $FeCl_3$	0.79% Fe_2O_3

The iron found in the leather is less than 1 per cent, whereas in the regular iron tannage, at least 4 per cent as Fe_2O_3 is found in the leather. According to Hou,[112] "To produce a satisfactory tannage, at least for a light leather, an amount of iron, calculated as Fe_2O_3, not less than 4 per cent of the weight of the air dried sample should be present." Besides, in the present investigation the amount of ferric chloride used in the tanning solution was very small in comparison with the organic tanning material, being in a ratio of about 8 parts of organic material to 1 part of ferric chloride, and in terms of the weight of raw hide, the amount of ferric chloride used was about 2 per cent for the tanning process. In fact, tanning with ferrric chloride alone has not been successful. The recent work of Moeller[113] on iron tannage showed that neither ordinary nor neutralized $FeCl_3$ solutions furnish a complete tanning system. On long time of action very great hydrolysis of the hide occurs, which is due to the great electrolytic dissociation of the iron salt.

From the above information, it is clear that the use of ferric chloride in connection with the naphthol derivatives is not a process of iron tannage, and the function of ferric chloride is solely that of a condensing, oxidizing or catalysing agent as has been discussed before.

Final Formulation of the Hydroxy Theory

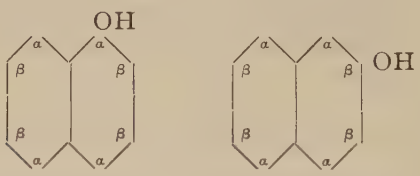
Criterion of the Hydroxy Theory

In the above investigation, it has been found that the hydroxy group (OH) is the primary tanning group for certain classes of compounds such as naphthalene derivatives and triphenylcarbinol derivatives, because it is impossible to get tannage with these compounds without the presence of the hydroxy group. In case of naphthalene derivatives, the hydroxy group is present in the original compound and in case of triphenyl-carbinol derivatives, the hydroxy group may be formed during the process of tanning. In either case the hydroxy group is the active tanning group as has been proven. On the other hand the theory does not assume that

[112] A Book, "Practical Tanning," by Allen Rogers, (1922), p. 224. Henry Carey Baird & Co., New York.

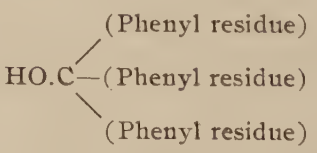
[113] Moeller, W., "Mineral Tannages," *Collegium*, (1921), 67-75, *Chemical Abstracts*, **15**, 2015, (1921).

all hydroxy compounds must have tanning properties, because they have hydroxy groups, for many compounds such as alcohols and simple phenols are known to have no tanning effects. Even in the family of simple naphthalene derivatives, only those from alpha-naphthol were found to tan, while those from beta-naphthol had no tanning effects. In studying the structural formulae of these compounds, it is observed that all those which have their hydroxy group at or near the center of the molecule have more or less tanning effects, while those which have their hydroxy group away from the center have little or no tanning properties. In the naphthalene rings, there are two central carbons, *i. e.*, the 9th and 10th carbons. Nearest to these two central carbons are the alpha carbons, and farther from the central carbons are the beta carbons. The results of the experiments show that when the hydroxy group is at an alpha position of the naphthalene rings, the compound has more or less tanning values, and that when the hydroxy group is at a beta position the compound does not tan. The structures of a-naphthol and b-naphthol are as follows:



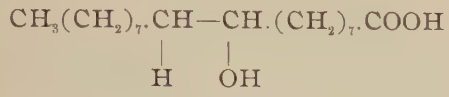
α-Naphthol β-Naphthol

In the case of triphenylcarbinol derivatives, the hydroxy group is at the center of the molecule as shown in the following:



The significance of the hydroxy group in the central position of the molecule is also shown in oil tannage, for Mathur[53] found that when the hydroxy group is near the carboxyl group, *i. e.*, near the end of the chain, the oil is incapable of chamoising the skin,

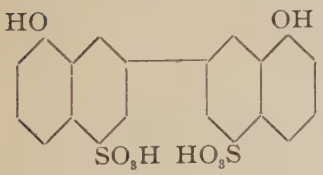
on the other hand when the hydroxy group is near the center of the chain, the oil has definite tanning effects, such as:



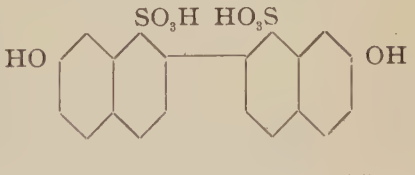
(Hydroxystearic acid)

The above facts all indicate the importance of the central position in the molecule where the hydroxy group derives its tanning property. It is obvious that if the hydroxy group is in the center, it is in the most balanced position of the molecule. The reason that the hydroxy group in such a position is the most active in tanning may be due to the fact that in the chemical combination of the hydroxy group with hide substance, the linkage at such a point yields the most stable compound.

It was found, again, that when the naphthol derivatives were condensed with ferric chloride, both alpha and beta naphthol derivatives became active tanning agents. It should be particularly noted that while the simple beta-naphthol derivatives had no tanning properties, they acquired them, by such condensation. The structures of these condensation products are known as follows:

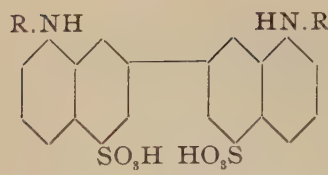


(Condensed L-Acid)

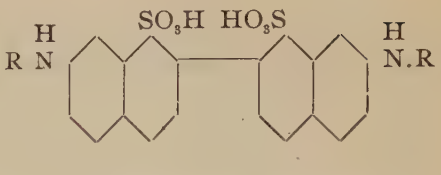


(Condensed Crocein Acid)

It is to be noted that the hydroxy groups are now at both ends of the molecule. Although the hydroxy groups are not at the center, they are in a balanced condition just the same, for in their combination with the amino groups of the hide substance, the molecule is tied up at both ends in a well balanced condition, as shown in the following:

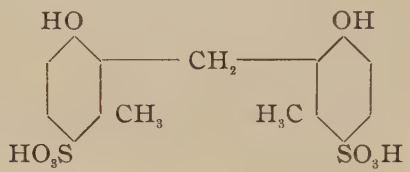


(Leather from Condensed L-Acid)

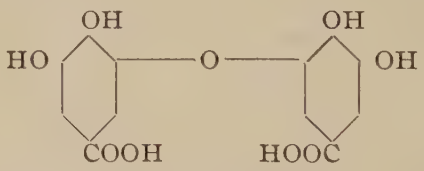


(Leather from Condensed Crocein Acid)

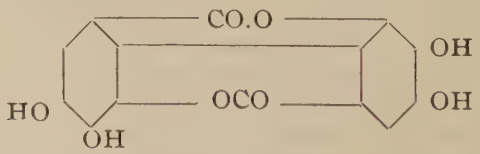
The condensation products of phenol derivatives and formaldehyde all have the structure in a balanced condition which can be represented by that of Neradol D.



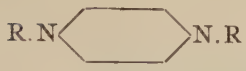
The digallic acid of Schiff is a condensation product in a balanced condition and represents a class of products involving the use of the condensing agents such as phosporus oxychloride, sulphur chloride and heat.



The vegetable tanning is said to be due to ellagic acid which again has its hydroxy groups in a balanced condition.



The tanning with quinones is also due to the presence of a balanced structure.



All these examples are only representatives of the different classes of tanning compounds which involve the principle of "balanced condition" or symmetrical location.

With the clear vision of the "balanced condition" in mind, the hydroxy theory of tanning can be expressed as follows:

When an organic compound has one or more than one hydroxy group in a "balanced condition" available for the formation of stable compounds with the hide substance, the compound and its derivatives will show more or less tanning effects, which can only be modified by the entering groups but not entirely nullified by them. The primary tanning group of these compounds is the hydroxy group or groups symmetrically located or in other words in a "balanced condition."

Influence of Other Groups on the Tanning Properties of the Hydroxy Groups in the Naphthalene Derivatives

It has been pointed out that all derivatives of a-naphthol are capable of converting raw hide into leather. However, it was found that the tanning effects of the a-naphthol derivatives are not the same, and are influenced by the entering groups, especially the acid and basic groups. In preparing synthetic tannins, it is almost a general process to introduce sulfonic groups into the compound. The purpose of this operation is two-fold. The first is to make the compound more soluble in water, so that the compound can be applied in water solutions. The second is that the sulfonic group possesses some sort of pickling action[110] and penetrates into the hide substance quickly, so as to furnish a lead for the organic tannins to come in contact with the hide substance more easily. As soon as these two functions are accomplished, the duty of the sulfonic groups is done, and the excess of the sulfonic groups is injurious to the process. In the first place, sulfonic groups will tend to swell the hide, producing a gelatinized skin, and in the second place it will dissolve some of the hide substance, causing a loss of leather. Other acidic groups such as Cl will diminish the tanning properties of hydroxy groups. How-

ever, such injurious acidic groups can be counterbalanced by introducing some basic groups such as NH_2 groups into the same rings, and these latter groups are beneficial as far as we have the injurious acidic groups present, and these points constitute the principle of "Balancing Effects of Acidic and Basic Groups," which has been fully discussed above. What is to be emphasized here is that the entering groups could only intensify or lessen the tanning properties of the active hydroxy groups, and would not entirely nullify them, for those a-naphthol derivatives which had been injured by too many sulfonic groups could be made to tan under special conditions.

Analogy Between Tanning Groups and Dyeing Groups

Here we find that there is an analogy between tanning and dyeing groups. In Witt's theory of "Chromophore and Auxochromes" for dye-stuffs, the chromophore is the fundamental principle for forming the dyestuff, and auxochromes are only modifiers of the dye-colors. As far as there is a chromophore group present in the organic compound, it is capable of being converted into dyestuffs, and for making dyes of different colors, any auxochromes may be chosen, depending on the desire of its manufacturer and on the applicability of the auxochromes. However, in the absence of chromophore, the auxochromes can produce no dyes. Quite similarly for the tanning groups, as far as the primary tanning group (OH) is holding a favorable position or in an activated state, the compound is capable of converting pelt into leather, and the entering groups will only influence in producing different grades of leather, as well as the colors of the leather. Just as the color of the chromophore is intensified or lightened by the entering auxochromes, the tanning effects of the primary tanning groups are strengthened or lessened by the presence of other groups. For the simple naphthalene derivatives, as far as there is a hydroxy group (OH) present in an alpha position in the double rings, the compound possesses tanning properties which are only modified by other groups such as sulfonic, amino, chloro, and carboxyl groups. But in the absence of an alpha hydroxy group, there is no tanning.

Activity of the Naphthol Groups and Further Proof of the Chemical Theory of Tanning

According to Richter,[114] phenols or naphthols can be directly converted into primary or secondary amines by heating with $ZnCl_2.NH_3$ to 300°-350° C. An easier reaction than that of the phenols is shown by the naphthols, and in the latter case pure ammonia may be employed.

$$\underset{\text{Naphthol}}{C_{10}H_7.OH} + NH_3 = C_{10}H_7.NH_2 + H_2O$$

In the light of this reaction, the chemical theory of tanning employed in the present investigation is firmly established, for the hide substance is but a form of substituted ammonia, and the reaction between the hydroxy group of the naphthol and the substituted ammonia (the hide substance) is much the same with the elimination of water, as follows:

$$\underset{\text{(a-Naphthol)}}{C_{10}H_7.OH} + \underset{\text{(Hide)}}{R\text{-}NH_2} = \underset{\text{(Leather)}}{C_{10}H_7.NH.R} + H_2O$$

In the tanning process, the reaction may be more complete so that all hydrogen atoms in the substituted ammonia are replaced by the tanning materials, thus:

$$2C_{10}H_7.OH + R\text{-}NH_2 = R\text{-}N:(C_{10}H_7)_2 + 2H_2O$$

In the tanning experiments, it was found that simple a-naphthol derivatives were much more active than the simple phenol derivatives. This is quite in accord with the chemistry of these two classes of compound, for Richter[115] found that in general the hydroxy group of the naphthols is much more reactive than the hydroxy group of the phenol.

Derived from this general knowledge of organic chemistry, and from other sources of information previously discussed, it can be concluded that tanning with certain aromatic hydroxy compounds is essentially a chemical process, as undoubtedly are most tanning phenomena.

[114] Richter's Organic Chemistry, English Translation by E. E. F. D'albe (1922), p. 81. P. Blakiston's Son & Co., Philadelphia.

[115] *Ibid.* p. 665.

VITA

Yun-Hua Li was born on February 5, 1900, at Kwei Shien, Kwangsi, China. After receiving his early education in Kwei Shien Middle School, Kwangsi, and in Ching Chong Middle School, Shanghai, he was admitted in 1917 by competitive examination into Tsing Hua College, Peking, from which institution he was graduated in the year 1921 with a scholarship to study in America. In the autumn of the same year he entered the University of Wisconsin, which conferred upon him the degree of B. S. in Chemistry in 1923. He came to attend the Engineering School of Columbia University in 1923 and completed the work for the degree of Ch. E. in 1925. During the next six months he studied leather manufacturing at Pratt Institute.

In 1920 he was with the Chinese Government Industrial Commission as technical translator. For some time he was analyst of various chemical products for commercial concerns. He is member of the Chinese Engineering Society, the Chinese Science Society, and the Chemical Society of China, serving as Secretary of the latter from 1925-1926.